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A TEXT-BOOK OF INORGANIC CHEMISTRY

VOLUME XI. PART III.

THE PERIODIC TABLE.*

Periods.	Group O.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
		1 H 1·0078							
First short period	*2* He 4·002	*3* Li 6·940	*4* Be 9·02	*5* B 10·82	*6* C 12·00	*7* N 14·008	*8* O 16·000	*9* F 19·00	
Second short period	*10* Ne 20·183	*11* Na 22·997	*12* Mg 24·32	*13* Al 26·97	*14* Si 28·06	*15* P 31·02	*16* S 32·06	*17* Cl 35·457	
First long period: Even series	*18* A 39·944	*19* K 39·10	*20* Ca 40·08	*21* Sc 45·10	*22* Ti 47·90	*23* V 50·95	*24* Cr 52·01	*25* Mn 54·93	*26* Fe 55·84 *27* Co 58·94 *28* Ni 58·69
First long period: Odd ,,		*29* Cu 63·57	*30* Zn 65·38	*31* Ga 69·72	*32* Ge 72·60	*33* As 74·91	*34* Se 78·96	*35* Br 79·916	
Second long period: Even series	*36* Kr 83·7	*37* Rb 85·44	*38* Sr 87·63	*39* Y 88·92	*40* Zr 91·22	*41* Nb 93·3	*42* Mo 96·0	*43* Ma ...	*44* Ru 101·7 *45* Rh 102·91 *46* Pd 106·7
Second long period: Odd ,,		*47* Ag 107·880	*48* Cd 112·41	*49* In 114·76	*50* Sn 118·70	*51* Sb 121·76	*52* Te 127·61	*53* I 126·92	
Third long period.	*54* Xe 131·3	*55* Cs 132·91	*56* Ba 137·6	*57* La 138·92	*58* Ce 140·13 *59* Pr 140·92	*60* Nd 144·27 *61* Il ...	*62* Sm 150·43 *63* Eu 152·0	*64* Gd 157·3 *65* Tb 159·2	
Fourth long period.		*66* Dy 162·46 *67* Ho 163·5	*68* Er 167·64 *69* Tm 169·4	*70* Yb 173·04 *71* Lu 175·0	*72* Hf 178·6	*73* Ta 181·4	*74* W 184·0	*75* Re 186·31	*76* Os 191·5 *77* Ir 193·1 *78* Pt 195·23
Fifth long period: Even series		*79* Au 197·2	*80* Hg 200·61	*81* Tl 204·39	*82* Pb 207·22	*83* Bi 209·00	*84* Po [210]	*85* ...	
Fifth long period: Odd ,,	*86* Rn 222	*87* ...	*88* Ra 225·97	*89* Ac ...	*90* Th 232·12	*91* Pa ...	*92* U 238·14		

* The Revised International Atomic Weights for 1934 are adopted in this Table as accepted by the Council of the Chemical Society.

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A TEXT-BOOK OF INORGANIC CHEMISTRY.

EDITED BY
J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
CARNEGIE GOLD MEDALLIST.

VOLUME XI.

ORGANOMETALLIC COMPOUNDS.

PART III.

DERIVATIVES OF PHOSPHORUS, ANTIMONY AND BISMUTH.

BY
ARCHIBALD EDWIN GODDARD, M.Sc. (B'ham).

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GENERAL INTRODUCTION TO THE SERIES.

During the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches : namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned ; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the original scheme, in addition to a detailed account of the elements of Group O, the general principles of Inorganic and Physical Chemistry were discussed in Volume I. It was later felt, however, that this arrangement was hardly satisfactory, and an Introduction to these principles is now afforded by my Text-book of Physical Chemistry, Volumes I. and II. (1932–35), whilst in future editions Volume I. of this Series will deal with the Inert Gases alone.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX.

under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferrocyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicals and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing to the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:—

Hydrogen	= 1·00762.	Oxygen	= 16·000.
Sodium	= 22·996.	Sulphur	= 32·065.
Potassium	= 39·100.	Fluorine	= 19·015.
Silver	= 107·880.	Chlorine	= 35·457.
Carbon	= 12·003.	Bromine	= 79·916.
Nitrogen	= 14·008.	Iodine	= 126·920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and, moreover, it renders the data for the different elements strictly comparable throughout the whole series.

Since the original scheme was drawn up in 1912, enormous progress has been made in all branches of chemistry, and the original intention of devoting one book only to each Vertical Group in the Periodic Table has had to be abandoned. In several cases it has been necessary to devote a whole book to a single element, as, for example, in the cases of oxygen, nitrogen, phosphorus and arsenic. Further, a separate volume has been devoted to the Metal-Ammines and a comprehensive account of the Organometallic Derivatives is given in Volume XI., which is being issued in four parts.

The Editor would draw attention to the unsatisfactory state of the nomenclature of organometallic compounds in general. The designations of compounds in Volume XI. are those used in the original memoirs, since any attempt to alter these in a work of that description would only complicate matters.

Our aim has not been to make the volumes absolutely exhaustive,

as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xvii–xix.

The addition of the *Table of Dates of Issue of Journals* (pp. xxi–xxviii) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the Authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

November 1935.

PREFACE.

The present work deals with the organometallic derivatives of phosphorus, antimony and bismuth, and it is the first time these compounds of phosphorus and bismuth have been reviewed in detail. Some 2,600 phosphorus derivatives are described in the following pages. The antimony section deals with about 700 compounds, whilst the bismuth compounds number just over 100.

The author desires to thank Professor G. T. Morgan, O.B.E., LL.D., F.R.S., for reprints and permission to use figs. 1, 3, 4, 5; also the Royal Society for permission to reproduce figs. 1 and 3, and the Chemical Society figs. 2, 4 and 5; Dr. W. J. Jones for reprints and permission to use fig. 2; Professor F. Challenger, D.Sc., for reprints; and Dorothy Goddard, M.Sc., for help with the index.

A. E. GODDARD.

"Thallia,"
Glenfield Frith Drive,
Groby Road,
Leicester,
November 1935.

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LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
Afhandl. Fys. Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914+).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique (Paris) (1816–1913).
Ann. Mines	Annales des Mines.
Ann. Pharm.	Annalen der Pharmacie (1832–1839).
Ann. Phys. Chem.	Annalen der Physik und Chemie (1819–1899).
Ann. Physik	Annalen der Physik (1799–1818, and 1900+).
Ann. Physik, Beibl.	Annalen der Physik, Beiblättes.
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbeiten Kaiserl. Gesundheitsamte	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
Arch. exp. Pathol. Pharmak.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles, Genève.
Atti Acc. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
B.A. Reports	British Association Reports.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Akad. Ber.	See *Sitzungsber. K. Akad. Wiss. Berlin.*
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bot. Zeit.	Botanische Zeitung.
Bul. Soc. Stünte Cluj.	Buletinul Societâtei de Stünte din Cluj.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. de Belg.	Bulletin de la Société chimique Belgique.
Bull. Sci. Pharmacol	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. min. de France	Bulletin de la Société minéralogique de France.
Bull. U.S. Geol. Survey	Bulletins of the United States Geological Survey.
Centr. Min.	Centralblatt für Mineralogie.
Chem. Ind.	Die Chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Crell's Annalen	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
Dingl. poly. J.	Dingler's polytechnisches Journal.

Abbreviated Title.	Journal.
Drude's Annalen	Annalen der Physik (1900–1906).
Electroch. Met. Ind.	Electrochemical and Metallurgical Industry.
Eng. and Min. J.	Engineering and Mining Journal.
Gazzetta	Gazzetta chimica italiana.
Gehlen's Allg. J. Chem.	Allgemeines Journal der Chemie.
Geol. Mag.	Geological Magazine.
Gilbert's Annalen	Annalen der Physik (1799–1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Helv. Chim. Acta	Helvetica Chim. Acta.
Int. Zeitsch. Metallographie	Internationale Zeitschrift für Metallographie.
Jahrb. kk. geol. Reichsanst.	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch für Mineralogie.
Jahresber.	Jahresbericht über die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift für Naturwissenschaft.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Gasbeleuchtung	Journal für Gasbeleuchtung.
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Metals	Journal of the Institute of Metals.
J. Miner. Soc.	Mineralogical Magazine and Journal of the Mineralogical Society.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (*Petrograd*).
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Mem. Coll. Sci. Kyōtō.	Memoirs of the College of Science, Kyōtō Imperial University.
Mém. Paris Acad.	Mémoirs présentés par divers savants à l'Académie de Sciences de l'Institut de France.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. scient.	Moniteur scientifique.
Münch. Med. Wochenschr.	Münchener Medizinische Wochenschrift.
Nature	Nature.
Nuovo Cim.	Il nuovo Cimento.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Öfvers. K. Vet.-Akad. Förh.	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Post	Pharmazeutische Post.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie (1824–1877).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Phil. Soc. Glasgow	Proceedings of the Royal Philosophical Society of Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.

Abbreviated Title.	Journal.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Roy. Inst. Reports	Reports of the Royal Institution.
Schweigger's J.	Journal für Chemie und Physik.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich-Preussischen Akademie de Wissenschaften zu Berlin.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
Techn. Jahresber.	Jahresbericht über die Leistungen der Chemischen Technologie.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trav. et Mém. du Bureau intern. des Poids et Mes.	Travaux et Mémoires du Bureau International des Poids et Mesures.
Verh. Ges. deut. Naturforsch. Aerzte.	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie (1877–1899).
Wissenschaftl. Abhandl. phys.-tech. Reichsanst.	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Chem.	Kritische Zeitschrift für Chemie.
Zeitsch. Chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie.

TABLE OF DATES OF ISSUE OF JOURNALS.

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year.	Amer. J. Sci.	Ann. Chim. Phys.	Ann. Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	...	(1) 32–35	...	...	...	4–6	...	5–8	90	...
1	...	36–39	...	...	...	7–9	...	8–11	91	...
2	...	40–43	...	...	...	10–12	...	11–14	92	...
3	...	44–47	...	...	...	13–15	...	14–17	93	...
4	...	48–51	...	...	...	16–18	...	17–20	94	...
1805	...	52–55	...	...	...	19–21	...	20–23	95	...
6	...	56–60	...	...	...	22–24	...	23–26	96	...
7	...	61–64	...	...	...	25–27	...	26–29	97	...
8	...	65–68	...	...	...	28–30	...	29–32	98	...
9	...	69–72	...	...	...	31–33	(1) 1*	33, 34	99	...
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11	...	77–80	...	...	...	37–39	3	37, 38	101	...
12	...	81–84	...	...	...	40–42	4	39, 40	102	...
13	...	85–88	...	...	...	43–45	5	41, 42	103	...
14	...	89–92	...	...	...	46–48	6	43, 44	104	...
1815	...	93–96	...	...	...	49–51	(2) 1	45, 46	105	...
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1830	17, 18	...	43–45	7–8	31–34	...	...	35–38	16	...	...	7, 8	120	18–20	...	...	...
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49	7, 8	69–72	25–27	15, 16	57–60	...	28, 29	111–114	15, 16	46–48	...	34, 35	139	76–78	...	2, 3	2, 3
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1870	...	49, 50	...	153–156	7	19–21	17, 18	141–144	3	13, 14	21, 22	...	...
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74	...	7, 8	...	171–174	..	(5) 1–3	5, 6	204, 205	7	21, 22	29, 30	...	...
1875	...	9, 10	...	175–179	...	4–6	7, 8	206, 207	8	23, 24	31, 32	...	...
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1860	50, 51	155–158	...	...	...	37, 38	79–81	...	...	...	4	...	19, 20
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1860	150	109–111	...	10, 11	13	...	39–42	...	...	...	...	...	...
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1865	155	124–126	...	14	...	...	51, 52	...	...	4	...	...	...
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1870	160	139–141	...	18, 19	...	...	61, 62	...	...	9	...	...	...
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1915	ceased	39, 40	40	...	...	...	253	48	17, 18	111, 112	56, 57	12	39	160, 161
16	...	41, 42	41	...	...	...	254	49	19, 20	113, 114	58, 59	13	40	162, 163
17	...	43, 44	42	...	...	...	255	50	21, 22	115, 116	60, 61	14	41	164, 165
18	...	45, 46	43	...	...	...	...	51	23, 24	117	62, 63	15	42	166, 167
19	...	47, 48	44	...	...	...	...	52	25, 26	118, 119	64, 65	16	43	168, 169

Year.	Dingl. poly. J.	Gazzetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Ind. Eng. Chem.	J. Pharm. Chim.	J. Physical Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon.* scient.	Nature.	Phil. Mag.
1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279–282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283–286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287–290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291–294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295–298	25	17	67, 68	...	(6) 1, 2	...	51, 52	27	14	16	45, 46	51, 52, 53	39, 40
96	299–302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53, 54, 55	41, 42
97	303–306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55, 56, 57	43, 44
98	307–310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311–314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
1	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6) 1, 2
2	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
3	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
4	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
6	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
7	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
8	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
9	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79–82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82–85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85–88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100–102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102–104	37, 38

* See footnote, p. xxii.

Year.	Phil. Trans.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. anorg. Chem.	Zeitsch. Elektro-chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1890	A. 181	...	6	47, 48, 49	9	99	10	39–41	29	3	...	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42–44	30	4	...	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48–50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186	...	11	57, 58, 59	14	104	15	54–56	34	8	8–10	1, 2	24, 25	16–18
96	187, 188	...	12	59, 60	15	105	16	57–59	35	9	11, 12, 13	2, 3	26–28	19–21
97	189, 190	...	13	60, 61, 62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	14	62, 63, 64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	...	15	64, 65, 66	18	108	19	67–69	38	12	19–22	5, 6	31, 32	28–31
1900	194, 195	1	16	66, 67	19	109	20	Con-	39	13	22–25	6, 7	32–34	32–35
1	196, 197	2	17	68, 69	20	110	21	tinued as	40	14	26–29	7	34–36	36–38
2	198, 199	3	18	69, 70	21	111	22	Annalen	41	15	29–33	8	36, 37	39–42
3	200–202	4	19	71, 72	22	112	23	der	42	16	33–37	9	37–39	43–46
4	203	5	20	72, 73, 74	23	113	24	Physik.	43	17	38–42	10	39, 40	47–49
1905	204, 205	6	21	74–76	24	114	25		44	18	43–48	11	40–42	50–53
6	206	7	22	A. 77, 78	25	115	26		45	19	48–52	12	42, 43	54–57
7	207	8	23	78, 79, 80	26	116	27		46	20	52–56	13	43, 44	58–60
8	207–209	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
9	209, 210	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
1910	210	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69–73	17	49, 50	75–77
12	211, 212	13	28	86, 87	31	121	32		51	25	73–79	18	50–52	78–80
13	212, 213	14	29	88, 89	32	122	33		52	26	79–83	19	52, 53	81–86
14	213, 214	15	30	89, 90	33	123	34		53	27	84–90	20	54	86–88
1915	215, 216	16	Publication	...	34	...	35		54	28	90–93	21	55	89, 90
16	216, 217	17	of matter	...	35	...	36		55	29	94–98	22	...	91, 92
17	217	18	of scientific	...	36, 37	...	37		56	30	99–101	23	...	92
18	217	...	interest now	...	37	...	38		57	31	102–104	24	No	92
19	...	...	abandoned.	...	38	...	39		58	32	105–109	25	issue*	...

* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOLUME XI. PART III.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. XI. PART III. ORGANOMETALLIC COMPOUNDS.

CHAPTER I.

ALIPHATIC PHOSPHORUS COMPOUNDS.

Compounds of the Type RPH_2.

The primary alkyl phosphines may be prepared by the general method indicated by the following equations :

$$2RI + 2PH_4I + ZnO = 2RPH_2.HI + ZnI_2 + H_2O$$
$$2RI + PH_4I + ZnO = R_2PH.HI + H_2O + ZnI_2$$

The main product of the reaction is a primary phosphine, but some secondary phosphine is obtained as a by-product. The reaction takes place when the components are heated together in a sealed tube at about 150° C. ; *n*-octylphosphine, however, requires a temperature of 160° to 180° C. to complete the reaction. Methylphosphine is a gas, and the remaining six members of the class which have been prepared are transparent liquids. The lower members have extremely obnoxious odours, the pungency decreasing somewhat with rising molecular weight. With the exception of the *iso*amyl- and *n*-octyl-derivatives all have boiling-points below 100° C. There is a tendency towards inflammation in contact with air in the case of the lower members, and fuming nitric acid may cause inflammation and formation of the corresponding phosphinic acid. Chlorine and bromine react with sufficient violence to cause inflammation in the case of the methyl- and ethyl-derivatives. Halogen acids combine with the phosphines, forming salts which have well-defined crystalline forms.

Methylphosphine, $CH_3.PH_2$, may be obtained in several ways : (1) A mixture containing one part of zinc oxide, two parts of phosphonium iodide and two parts of methyl iodide is heated for four hours in a sealed tube at 150° C.[1] The reaction produces both primary and secondary phosphines, which are separated as follows : The reaction mass is treated with water in an atmosphere of hydrogen, whereby methylphosphine is liberated from the hydriodide, whilst the residue contains the zinc iodide double salt of dimethylphosphonium iodide.

[1] Hofmann, *Ber.*, 1871, 4, 605.

(2) By the action of methyl iodide on a solution of white phosphorus in sodium hydroxide.[1] The product in this case is contaminated with secondary and tertiary phosphines. (3) By heating for several hours at about 250° C., 1 gram-atom of white phosphorus with 2 gram-molecules of methyl alcohol in a sealed tube, the following by-products also occurring: phosphine, phosphoric acid, phosphinic acids and tetramethylphosphonium hydroxide.[2] (4) By heating a mixture of phosphonium iodide, zinc oxide and chloroform at 100° C.[3]

Methylphosphine is a colourless, transparent gas, having a vile odour. It begins to liquefy at 0° C. at 1·75 atmospheres pressure, the liquid being colourless and mobile, B.pt. −14° C. at 758·5 mm.[4] It is practically insoluble in water, somewhat soluble in alcohol, and one volume of ether at 0° C. dissolves 70 volumes of methylphosphine. It readily oxidises and forms white fumes in contact with the air, soon catching fire, particularly on gentle warming. In contact with chlorine or bromine it burns with a brisk flame. When passed into fuming hydrochloric acid or mixed with hydrogen chloride it yields the *hydrochloride*, $CH_3.PH_2.HCl$, which crystallises in four-sided plates. These are volatile in ether vapour; their solution in concentrated hydrochloric acid gives an orange-red *platinichloride*. In a similar way a *hydriodide* may be obtained which crystallises in plates and may be sublimed in a current of dry hydrogen. When passed into fuming nitric acid, methylphosphine is converted into methylphosphinic acid.

Ethylphosphine, $C_2H_5.PH_2$.—This is prepared by the following methods: (1) A mixture of one part of zinc oxide, four parts of phosphonium iodide and four parts of ethyl iodide is digested for six to eight hours at a temperature not exceeding 150° C.[5] The reactions taking place are as follows:

$$2C_2H_5I + 2PH_4I + ZnO = 2C_2H_5.PH_2.HI + ZnI_2 + H_2O$$
$$2C_2H_5I + PH_4I + ZnO = (C_2H_5)_2.PH.HI + H_2O + ZnI_2$$

The chief product is primary phosphine, which is liberated in a hydrogen-filled apparatus by slowly heating to boiling in a stream of hydrogen and pouring the boiling liquid into cold water. The oil which separates is primary phosphine and is dried over potassium hydroxide. (2) Ethylene dibromide, phosphonium iodide and zinc oxide are heated for six hours at 160° C.[6] (3) One gram-atom of white phosphorus and 2 gram-molecules of alcohol are heated in a sealed tube for many hours at about 250° C., the following by-products also occurring: phosphine, phosphinic acids, phosphoric acid and tetraethylphosphonium hydroxide.[7]

The phosphine is a colourless, strongly refracting liquid, having a very objectionable odour. It boils at about 25° C., is lighter than water and insoluble in it. The vapour attacks cork and rubber, and in contact with chlorine, bromine or fuming nitric acid the phosphine inflames. It combines with sulphur, yielding a non-crystalline substance. With concentrated halogen acids it forms salts, the *hydro-*

[1] Auger, *Compt. rend.*, 1904, 139, 640, 671.
[2] Berthaud, *Compt. rend.*, 1906, 143, 1166.
[3] Hofmann, *Ber.*, 1873, 6, 302.
[4] Hofmann, *ibid.*, 1871, 4, 608.
[5] Hofmann, *ibid.*, 1871, 4, 430; Hofmann and Mahla, *ibid.*, 1892, 25, 2437.
[6] Hofmann, *ibid.*, 1873, 6, 302.
[7] Berthaud, *loc. cit.*

chloride forming a *platinichloride* which separates in carmine-red needles. The *hydriodide* crystallises in white, four-sided plates, subliming in a hydrogen atmosphere at 100° C. The salt is decomposed by water, but can be kept unchanged in dry air; it dissolves in alcohol, but decomposition soon sets in, and it is insoluble in ether, the only solvent in which it is perfectly stable being concentrated hydriodic acid. The addition of ether to such a solution causes the precipitation of the hydriodide in crystals 1 cm. in length. When an ether solution of phosphine and cyanogen chloride is heated for several hours at 100° C., rhombic plates are isolated from the reaction mixture; these melt at 49° to 50° C. and correspond to the formula, $C_2H_5.PH(CN)$.[1]

n-Propylphosphine, $CH_3.CH_2.CH_2.PH_2$.—This is prepared by heating a mixture of 21·25 grams of propyl iodide, 20·25 grams of phosphonium iodide and 5·1 grams of zinc oxide in a sealed tube at 160° to 170° C. The reaction product is then decomposed by water to separate the primary from the secondary phosphine which occurs as a by-product.[2] The phosphine is a colourless liquid of disagreeable odour, B.pt. 53° to 53·5° C., inflaming in air.

iso-Propylphosphine, $(CH_3)_2.CH.PH_2$.[3]—This phosphine is obtained in the usual manner by heating 2 gram-molecules of *iso*propyl iodide, 2 gram-molecules of phosphonium iodide and 1 gram-molecule of zinc oxide in a sealed tube at 100° C., and decomposing the reaction mass with water. It boils at 41° C., and is lighter than and insoluble in water.

iso-Butylphosphine, $(CH_3)_2CH.CH_2.PH_2$, occurs when the *iso*propyl iodide in the preceding preparation is replaced by *iso*butyl iodide. It is a liquid, B.pt. 62° C.

iso-Amylphosphine, $C_5H_{11}.PH_2$, is prepared by heating *iso*amyl iodide, phosphonium iodide and zinc oxide in a sealed tube at 140° to 150° C. It has also been obtained by heating *iso*amyl phosphinous acid at 60° to 135° C., *iso*amylphosphinic acid occurring as a by-product.[4] The phosphine occurs also when *iso*amyl iodide reacts with a solution of white phosphorus in alcoholic sodium ethylate.[5] It is a liquid, B.pt. 106° to 107° C.,[6] 106° to 108° C.[7] It is oxidised to *iso*amylphosphinic acid by nitric acid, the mixture inflaming.

n-Octylphosphine, $CH_3.(CH_2)_6.CH_2.PH_2$.[8]—*n*-Octyl iodide, phosphonium iodide and zinc oxide are heated in a sealed tube at 160° to 180° C. The phosphine is a transparent, mobile, highly refractive liquid, having a pungent odour. It boils at 184° to 187° C., and has a density of 0·829 at 17° C. In alcohol, benzene or chloroform it readily dissolves, but is insoluble in water and mineral acids. It is violently attacked by fuming nitric acid unless previously diluted with glacial acetic acid, a spermaceti-like mass resulting. The phosphine slowly absorbs oxygen, forming *n*-octylphosphinous acid, which gives a white curdy silver salt. With hydriodic acid the *hydriodide* results as a crystalline solid, soluble in ether.

[1] Darmstädter and Henniger, *Ber.*, 1870, 3, 179.
[2] Partheil and Gronover, *Arch. Pharm.*, 1903, 241, 411.
[3] Hofmann, *Ber.*, 1873, 6, 294.
[4] Guichard, *Ber.*, 1899, 32, 1572.
[5] Auger, *Compt. rend.*, 1904, 139, 641.
[6] Hofmann, *loc. cit.*
[7] Guichard, *loc. cit.*
[8] Möslinger, *Ber.*, 1876, 9, 1005; *Annalen*, 1877, 185, 65.

Compounds of the Type R_2PH.

The preparation of the dialkyl phosphines has already been indicated in connection with the primary phosphines on p. 3. The lower members are spontaneously inflammable in air and combine with sulphur, while all combine readily with acids to form salts.

Dimethylphosphine, $(CH_3)_2PH$.[1]—This occurs as described under methylphosphine, p. 4. It is a colourless liquid, B.pt. 25° C., lighter than water and insoluble in it. When dissolved in hydrochloric acid it may be oxidised to dimethylphosphinic acid by means of fuming nitric acid. It is easily oxidised and inflames in air. It readily combines with acids, all the salts being easily soluble. The *hydrochloride* yields a crystalline *platinichloride*. The phosphine unites with sulphur and carbon disulphide.

Diethylphosphine, $(C_2H_5)_2PH$.[2]—This is prepared according to the equations given under ethylphosphine (p. 4). It is a colourless, strongly refractive, mobile liquid, B.pt. 85° C. It has a penetrating odour and is lighter than water. Its ether solution reacts with sulphur, forming *diethyldithiophosphine sulphide*, $(C_2H_5)_2PS.S.S.S.PS(C_2H_5)_2$, which is converted by ammonium sulphide into *ammonium diethyldithiophosphinate*, $(C_2H_5)_2PS.S.NH_4$. The phosphine dissolves in acids, but with the exception of the *hydriodide*, the salts are difficult to crystallise. The *hydrochloride* yields an orange-yellow *platinichloride*, crystallising in prisms. The salts are stable towards water.

Di-isopropylphosphine, $[(CH_3)_2CH]_2PH$,[3] occurs when *iso*propyl iodide, phosphonium iodide and zinc oxide are heated together at 100° C. The phosphine boils at 118° C., is lighter than water and insoluble in it.

Di-isobutylphosphine, $[(CH_3)_2.CH.CH_2]_2PH$, is a liquid, B.pt. 153° C., prepared in a similar manner to the preceding derivative.

Di-isoamylphosphine, $(C_5H_{11})_2PH$. — *iso*Amyl iodide, phosphonium iodide and zinc oxide yield this phosphine when heated together at 140° to 150° C. The phosphine is a liquid, B.pt. 210° to 215° C.

Compounds of the Type R_3P.

The trialkyl phosphines may be prepared in a variety of ways :

(1) By treating magnesium alkyl halides with phosphorus trihalides :

$$3RMgX + PX_3 = R_3P + 3MgX_2$$

(2) The double salts formed by the interaction of zinc dialkyls and phosphorus trihalides yield tertiary phosphines on treatment with potassium hydroxide :

$$3ZnR_2 + 2PX_3 = 2R_3P + 3ZnX_2$$

(3) By heating alloys of sodium and phosphorus with alkyl halides :

$$Na_3P + 3RI = R_3P + 3NaI$$

(4) The action of heat on a mixture of secondary phosphine and alkyl iodide, and treatment of the product with alkali, has produced

[1] Hofmann, *Ber.*, 1871, **4**, 605.
[2] Hofmann, *ibid.*, 1871, **4**, 433; Hofmann and Mahla, *ibid.*, 1892, **25**, 2437.
[3] Hofmann, *ibid.*, 1873, **6**, 294.

certain trialkyl phosphines containing secondary radicals, *e.g.* tri-*iso*-propylphosphine. The yields are not good and the products are somewhat impure :

$$R_2PH + RI = R_3P.HI$$

(5) When phosphonium iodide and an alcohol are digested for a long period at a high temperature, a mixture of trialkylphosphine hydriodide and tetra-alkylphosphonium iodide results :

$$PH_4I + 3R.OH = R_3P.HI + 3H_2O$$
$$PH_4I + 4R.OH = R_4PI + 4H_2O$$

This method and the following one have only been applied to methyl and ethyl compounds.

(6) In this case the alcohol in the foregoing method is replaced by ether, the reaction then proceeding at a lower temperature :

$$2PH_4I + 3R_2O = 2R_3P.HI + 3H_2O$$
$$PH_4I + 2R_2O = R_4PI + 2H_2O$$

(7) Trimethylphosphine has been isolated according to the following equations, tetramethylphosphonium iodide occurring at the same time :

$$PH_3 + 3RI = R_3P.HI + 2HI$$
$$PH_3 + 4RI = R_4PI + 3HI$$

(8) When phosphonium iodide and carbon disulphide are heated together, trimethylphosphine hydriodide is formed :

$$3CS_2 + 4PH_4I = (CH_3)_3P.HI + 3H_2S + 3PSI$$

The mixed tertiary phosphines are obtained by subjecting mixed tetra-alkylphosphonium compounds to dry distillation :

$$(CH_3)(C_2H_5)_3PCl = (CH_3)(C_2H_5)_2P.HCl + C_2H_4$$

In all cases of mixed aliphatic tertiary phosphines given in the following pages an ethyl group is removed from the phosphonium compound used as starting material, although a heavier group may be present in the molecule.

All the tertiary phosphines are highly refractive liquids, lighter than and insoluble in water. Those of low molecular weight readily absorb oxygen from the air, yielding oxides ; they also have indescribably unpleasant odours. The compounds combine with sulphur, selenium and carbon disulphide, forming respectively sulphides, selenides and compounds of the type

$$R_3P{-}{-}CS$$
$$\diagdown S \diagup$$

Mercuric chloride and the chlorides of gold, platinum and palladium form double compounds with some of the phosphines. Combination of the phosphines with alkyl iodides forms tetra-alkylphosphonium compounds :

$$R_3P + RI = R_4PI$$

Trialkylphosphine Oxides.—These compounds result when the trialkyl phosphines are oxidised directly by atmospheric oxygen, or

by nitric acid or mercuric oxide. Decomposition of tetra-alkylphosphonium hydroxides by heat also yields the oxides. A more general method consists in treating phosphorus oxychloride with magnesium alkyl halides, the reaction mixture subsequently being decomposed by hydrochloric acid. The oxides form many double compounds with metallic salts and organic acids.

Trialkylphosphine Sulphides and Selenides.—When an ether solution of a trialkylphosphine is treated with flowers of sulphur, the latter gradually disappears, removal of the solvent and boiling of the residue with water then giving the sulphide in crystalline form. The ethyl compound has also been obtained by the interaction of triethylphosphine and ethyl mercaptan in the presence of air. The selenides are prepared in a similar manner, but are rather unstable on exposure to the air.

Trimethylphosphine, $(CH_3)_3P$, may be prepared as follows: (1) Methyl chloride is passed over a phosphorus-calcium alloy, dimethylphosphorus, $[(CH_3)_2P]_x$, being formed at the same time.[1] (2) By the action of methyl iodide on a phosphorus-sodium alloy, the by-products being dimethylphosphorus and tetramethylphosphonium iodide.[2] (3) By the interaction of phosphorus trichloride and zinc dimethyl.[3] This reaction is dangerous to carry out and the containing vessels should be well cooled and kept full of carbon dioxide during the reaction, which takes place readily and lasts for several hours. Two layers of liquid are formed, and the lower one is withdrawn and distilled with potassium hydroxide, which releases the phosphorus base from its zinc compound. The phosphine passes over in the steam and collects in the receiver on the surface of the water, from which it is separated, and after drying over solid potassium hydroxide it is distilled in a current of dry hydrogen. (4) By saturating methyl iodide at $-10°$ C. with phosphine and heating to 100° C., or treating 1 volume of methyl iodide with 1 volume of a saturated ether solution of zinc iodide, cooling to $-10°$ C. and saturating the mixture with phosphine. Shining crystals of the zinc iodide double compound are obtained, these being treated with potassium hydroxide as before. In the first of these two processes the crystals separating out are probably a phosphonium compound.[4] (5) One part of carbon disulphide and three parts of phosphonium iodide are heated in a sealed tube at 140° to 150° C.[5] (6) The hydriodide of trimethylphosphine is formed when phosphonium iodide and dimethyl ether are heated together in a sealed tube for one to two hours at 120° to 140° C., tetramethylphosphonium iodide occurring as a by-product.[6] (7) The hydriodide also occurs when one molecular equivalent of phosphonium iodide and three molecular equivalents of methyl alcohol are heated in a sealed tube for six to eight hours at 160° to 180° C., the by-product being tetramethylphosphonium iodide.[7]

[1] Thénard, *Jahresber.*, 1847–1848, p. 645; *Compt. rend.*, 1847, 25, 892; *Phil. Mag.*, 1848, [3], 32, 153.

[2] Cahours and Hofmann, *Annalen*, 1857, 104, 1.

[3] Hofmann and Cahours, *Trans. Chem. Soc.*, 1859, 12, 56; Cahours and Hofmann, *loc. cit.*

[4] Drechsel and Finkelstein, *Ber.*, 1871, 4, 352; Hofmann, *ibid.*, 1871, 4, 372.

[5] Drechsel, *J. prakt. Chem.*, 1874, [2], 10, 180.

[6] Fireman, *Ber.*, 1897, 30, 1088.

[7] Hofmann, *Ber.*, 1871, 4, 205.

Trimethylphosphine is a colourless, transparent, very mobile liquid of exceedingly unpleasant odour. It boils at 40° to 42° C., is highly refractive, and lighter than and insoluble in water. In contact with the air it fumes and is apt to inflame, oxidation taking place with formation of its oxide. It combines also with sulphur and selenium, the operation being conducted in ether solution. It yields the following *platinichlorides*: $[(CH_3)_3P]PtCl_2$, crystallising from ether or alcohol in yellow prisms;[1] $Cl[(CH_3)_3P]Pt[(CH_3)_3P]Cl$, white crystals, insoluble in ether; $2(CH_3)_3P.2HCl.PtCl_4$, an orange-yellow crystalline precipitate.[2] The phosphine combines with *carbon disulphide*, yielding a red crystalline *compound*, $(CH_3)_3P{-}{-}CS$.[3] The condensation is brought about

simply by mixing the components or using an alcohol solution of the phosphine. The compound has similar properties to the corresponding ethyl compound, p. 10. Ether solutions of the derivative, when allowed to stand for twenty-four hours are gradually converted into trimethylphosphine sulphide. The phosphine forms *compounds* with *methylene iodide*, *ethylene*, *propylene* and *amylene bromides*,[4] and *ethyl*, *ethylene*, *allyl* and *phenyl thiocyanates*. Trimethylphosphine does not react with zinc ethyl,[5] which distinguishes it from primary and secondary phosphines, which are readily attacked. It combines with monochloracetic acid to yield a *betaine*, see p. 44.[6]

Triethylphosphine, $(C_2H_5)_3P$, is prepared in a variety of ways: (1) By the action of phosphorus-sodium alloy on ethyl iodide.[7] (2) A double compound of the phosphine with zinc chloride is produced when zinc diethyl reacts with phosphorus trichloride.[8] (3) The phosphine is formed together with its oxide when zinc diethyl reacts with phosphorus oxychloride.[9] (4) By heating 1 molecular equivalent of phosphonium iodide with 3 molecular equivalents of ethyl alcohol for 6 to 8 hours at 160° to 180° C., tetraethylphosphonium iodide occurring as a by-product. This process yields the hydriodide of the phosphine.[10] (5) By decomposition with potassium hydroxide of the base formed when a zinc phosphide, PHZn (prepared by the action of phosphine on zinc diethyl at a temperature not exceeding −4° C.), is heated with ethyl iodide in a sealed tube for 1½ hours at 150° C.[11] (6) By heating phosphonium iodide and diethyl ether together in a sealed tube for 6 hours at 160° C., tetraethylphosphonium iodide being formed as a by-product.[12] (7) By the decomposition of tetraethylphosphonium acetate, benzoate or oxalate by heat.[13] (8) When phosphorus, ethyl

[1] Werner, *Zeitsch. anorg. Chem.*, 1893, 3, 318; Klason and Wanselin, *J. prakt. Chem.*, 1903, [2], 67, 41; Blomstrand, *Ber.*, 1871, 4, 51; Cahours and Gal, *Compt. rend.*, 1870, 71, 208; *Jahresber.*, 1870, p. 811.

[2] Hofmann, *Annalen*, 1857, 104, 30.

[3] Hofmann, *Annalen Suppl.*, 1861, 1, 59; see Hantzsch and Hibbert, *Ber.*, 1907, 40, 1508.

[4] Hofmann, *Jahresber.*, 1859, p. 372.

[5] Gal, *J. Pharm. Chim.*, 1883, [5], 7, 484; *Compt. rend.*, 1883, 96, 578.

[6] Meyer, *Ber.*, 1871, 4, 734.

[7] Berlé, *Jahresber.*, 1855, p. 290; *J. prakt. Chem.*, 1855, 66, 73; *Annalen*, 1856, 97, 334.

[8] Cahours and Hofmann, *Annalen*, 1857, 104, 1; Hofmann and Cahours, *Quart. J. Chem. Soc.*, 1859, 11, 56; Hofmann, *Phil. Trans.*, 1860, 150, 409.

[9] Pebal, *Annalen*, 1861, 120, 198.

[10] Hofmann, *Ber.*, 1871, 4, 205.

[11] Drechsel and Finkelstein, *Ber.*, 1871, 4, 352.

[12] Fireman, *Ber.*, 1897, 30, 1088.

[13] Letts and Collie, *Phil. Mag.*, 1886, [5], 22, 183.

iodide and zinc are heated together in a sealed tube at 160° C., the zinc iodide double salt of the hydriodide of the phosphine results, together with the zinc iodide double salt of tetraethylphosphonium iodide.[1] (9) The foregoing double salt of the phosphine also occurs when ethyl iodide and zinc phosphide are heated together in a sealed tube at 180° C.[2] (10) The best method of preparation is as follows: To the Grignard solution obtained from 48·6 grams of magnesium and 218 grams of ethyl bromide in 400 to 500 c.c. of ether, 60 grams of phosphorus tribromide in 75 c.c. of ether are added dropwise, the whole being cooled in ice and salt. When the action has subsided, the mixture is placed in an oil-bath and distilled in a stream of carbon dioxide, the phosphine being passed into a mixture of ether and carbon disulphide, when the red double compound, $(C_2H_5)_3P.CS_2$, is precipitated. Only about 6 per cent. of the phosphine distils with the ether, the remainder coming over at 160° to 200° C. In this preparation success depends upon using a large excess of magnesium ethyl bromide, when a yield of about 70 per cent. is obtained.[3]

Triethylphosphine is a colourless liquid, possessing a stupefying odour which resembles hyacinths when diluted. It boils at 127·5° C. at 744 mm., and has a density of 0·812 at 15° C.,[4] 0·80006 at 18·6° C.;[5] $n_D = 1{\cdot}45799$. It is insoluble in water but miscible with alcohol and ether, and its vapour forms a white cloud in air owing to oxidation. The heat of combustion at constant pressure is 1,249,700 calories and the heat of formation 142,100 calories.[6] Strips of paper soaked in triethylphosphine explode in contact with oxygen.[7] Slow oxidation yields triethylphosphine oxide,[8] and in the absence of water 1 molecular proportion of the phosphine absorbs 1 atomic proportion of oxygen.[9] Oxidation of the phosphine to the oxide may also be effected by nitric acid or mercuric oxide.[10] Sulphur and selenium are readily dissolved by ether solutions of triethylphosphine, yielding triethylphosphine sulphide and selenide respectively. The phosphine reacts violently with ethyl iodide, forming tetraethylphosphonium iodide, but only unstable compounds are produced with cyanogen bromide or iodide.[11] *Carbon disulphide* yields the *derivative* $(C_2H_5)_3P.CS_2$ when the components are brought together in ether or alcohol solution. The constitution of this compound is probably $(C_2H_5)_3P{<}\!\!\!-\!\!\!-\!\!\!>CS$ and the form of the crystals is monoclinic prismatic.[12] The product melts at 95° C., is insoluble in water, sparingly soluble in ether, more soluble in carbon disulphide and fairly soluble in warm alcohol. It forms a *methiodide*, M.pt. 96° to 97° C., decomposed by sodium hydroxide. Heating the base for some days in a sealed tube with water at 100° C.

[1] Hofmann, *Annalen Suppl.*, 1861, 1, 4.
[2] Cahours, *Annalen*, 1862, 122, 331.
[3] Hibbert, *Ber.*, 1906, 39, 160.
[4] Cahours and Hofmann, *loc. cit.*
[5] Zecchini, *Gazzetta*, 1893, 23, i, 100.
[6] Lemoult, *Compt. rend.*, 1909, 149, 556.
[7] Hofmann, *Annalen*, 1857, 104, 11.
[8] Hofmann, *Annalen Suppl.*, 1861, 1, 10.
[9] Compare Jorissen, *Zeitsch. physikal. Chem.*, 1897, 22, 35; Engler and Wild, *Ber.*, 1897, 30, 1673; Engler and Weissberg, *ibid.*, 1898, 31, 3055.
[10] Hofmann, *loc. cit.*; Hofmann and Mahla, *Ber.*, 1892, 25, 2436.
[11] Hantzsch and Hibbert, *Ber.*, 1907, 40, 1508.
[12] Sella, *Annalen Suppl.*, 1861, 1, 28; see Groth, *Ch. Kr.*, 3, 43.

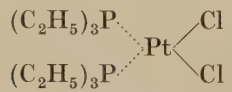
gives triethylphosphine sulphide, the oxide, methyltriethylphosphonium hydroxide, hydrogen sulphide and carbon monoxide.[1] Boiling with silver nitrate or silver oxide in alcohol solution converts the compound into triethylphosphine sulphide, and the latter also occurs when a saturated aqueous solution of hydrogen sulphide is heated with the carbon disulphide derivative at 100° C. in a sealed tube, a *product* $C_8H_{17}S_3P$ also being formed.[2] Heating with anhydrous fatty acids decomposes the carbon disulphide compound with formation of carbon oxysulphide, triethylphosphine and derivatives of thio-acids. Methyl iodide gives a red compound, M.pt. 96° to 97° C., having the structure $(C_2H_5)_3P{-}CS.S.CH_3I$.[3] The sulphur derivative, $C_7H_{15}S_2P$, may be considered to be the *anhydride of hydroxytriethylphosphonium dithiocarboxylic acid*, $HO.P(C_2H_5)_3CS.SH$, dry hydrogen chloride converting $C_7H_{15}S_2P$ into *chlorotriethylphosphonium dithiocarboxylic acid*, $Cl.P(C_2H_5)_3CS.SH$, a hygroscopic colourless, crystalline mass, stable in concentrated acid solution, but decomposed by water with evolution of hydrogen sulphide and deposition of sulphur. Alkali converts it into the anhydride, and platinic chloride yields a pale yellow, amorphous *platinichloride*, $2[Cl.P(C_2H_5)_3CS.SH].PtCl_4$, insoluble in alcohol and ether, soon undergoing decomposition at the ordinary temperature.[4] When the anhydride $C_7H_{15}S_2P$ is heated with saturated aqueous hydrogen sulphide, the product $C_8H_{17}S_3P$ is obtained. This forms yellow crystals, soluble in hot absolute alcohol but insoluble in ether, decomposed by hot water to give a compound, $C_7H_{18}SP(OH)$.[5] The corresponding iodide, $C_7H_{18}SP.I$, crystallises from water in needles, sparingly soluble in cold water; in aqueous solution it is decomposed by silver oxide, the precipitate containing silver, silver iodide and silver sulphide, whilst methyltriethylphosphonium hydroxide is found in solution. The compound formed from phenyl mustard oil and triethylphosphine decomposes on heating.[6] Carbon tetrabromide and triethylphosphine yield bromomethenyltri-triethylphosphonium bromide, $BrC[P(C_2H_5)_3Br]_3$. The corresponding chlorine compound is hydrolysed by water forming chloromethyltriethylphosphonium chloride, triethylphosphine oxide and hydrochloric acid:

$$ClC[P(C_2H_5)_3Cl]_3 + 2H_2O = Cl.CH_2.P(C_2H_5)_3Cl + 2(C_2H_5)_3PO + 2HCl$$

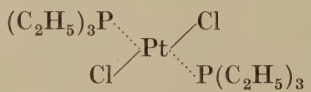
Triethylphosphine forms a large number of addition compounds with metallic salts, the constitution of some of the compounds having given rise to considerable discussion. The derivatives are as follows: From *auric chloride*—$(C_2H_5)_3P.AuCl$ or $[AuP(C_2H_5)_3]Cl$. This results when an alcohol solution of the phosphine is treated with auric chloride at the ordinary temperature.[7] It crystallises in colourless needles or prisms, melting with decomposition at 80° C., soluble in alcohol, ether, chloroform, benzene and acetic acid, sparingly soluble in warm water

[1] Hofmann, *loc. cit.* Compare Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 612.
[2] Hofmann, *Jahresber.*, 1861, p. 490.
[3] Hantzsch and Hibbert, *loc. cit.*
[4] Hofmann, *Annalen Suppl.*, 1861, **1**, 30.
[5] Hofmann, *Jahresber.*, 1861, p. 490.
[6] Staudinger and Meyer, *loc. cit.*
[7] Cahours and Gal, *Compt. rend.*, 1870, **70**, 1383; *Jahresber.*, 1870, p. 811; Levi-Malvano, *Atti R. Accad. Lincei*, 1870, [5], **17**, i, 852.

or carbon tetrachloride. The compound is very soluble in ammonium hydroxide or pyridine and dissolves without decomposition in warm potassium hydroxide and concentrated hydrochloric acid. If the compound in carbon tetrachloride solution be treated with ammonia, it is converted into a derivative having the constitution, $(C_2H_5)_3P.AuCl.2NH_3$ or $[AuP(C_2H_5)_3(NH_3)_2]Cl$. This crystallises from alcohol in colourless prisms, commencing to decompose at 90° C., yielding a white sublimate at 125° C., and blackening towards 150° C. It is only sparingly soluble in water. From *copper iodide*—$2(C_2H_5)_3P.CuI$. This product crystallises from petroleum ether in plates, M.pt. 37° to 39° C.[1] From *zinc iodide* — $2(C_2H_5)_3P.2HI.ZnI_2$. The derivative crystallises from water or alcohol.[2] From *palladium chloride*—$2(C_2H_5)_3P.PdCl_2$. The salt separates from alcohol or ether in yellow prisms, insoluble in water.[3] From *platinic chloride*—when triethylphosphine is boiled with an aqueous solution of platinic chloride, two isomeric *bistriethylphosphine dichloroplatinum compounds* are produced. They may be separated by treatment with ether, in which the *α-form* (yellow) is soluble, whilst the *β-form* (white) is insoluble.[4] The α-form separates from alcohol or ether in yellow, monoclinic prisms,[5] M.pt. 150° C., density 1·50 at 10° C., insoluble in water, sparingly soluble in boiling alcohol, readily dissolving in ether. Heating at 100° C. with alcohol or treating its ether solution with triethylphosphine converts the α-isomer into the β-variety. The α-form, when boiled with water and triethylphosphine, yields a *compound*, $4(C_2H_5)_3P.PtCl_2$, which readily splits off triethylphosphine, forming the β-isomer. The α-form can add on 1 molecule of bromine or iodine. The β-compound is obtained as described above and separates from boiling alcohol in prisms, insoluble in water or ether. It also adds on 1 molecule of bromine or iodine. The constitution of the isomers is probably as follows : [6]

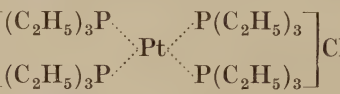


α-Modification



β-Modification

The complex $4(C_2H_5)_3P.PtCl_2$, mentioned above, has the structure :



This salt, when treated with *auric chloride*, yields a yellow crystalline *compound*, $4(C_2H_5)_3P.PtCl_2.AuCl_3$, and with *platinic chloride* a brown *precipitate* results, $4(C_2H_5)_3P.PtCl_2.PtCl_4$, sparingly soluble in cold alcohol.[7] A *platinichloride* of the composition $2(C_2H_5)_3P.H_2PtCl_6$ is known ; it is a crystalline product, sparingly soluble in cold water,

[1] Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 315; *Chem. Zentr.*, 1906, ii, 751.
[2] Hofmann, *Annalen Suppl.*, 1861, 1, 4; Cahours, *Annalen*, 1862, 122, 334.
[3] Cahours and Gal, *loc. cit.*
[4] Cahours and Gal, *Compt. rend.*, 1870, 70, 899; *Jahresber.*, 1870, p. 809.
[5] Des Cloizeaux, *Compt. rend.*, 1870, 70, 899; *Jahresber.*, 1870, p. 809; Sella, *Annalen Suppl.*, 1861, 1, 28; see Groth, *Ch. Kr.*, 3, 43.
[6] Werner, *Zeitsch. anorg. Chem.*, 1893, 3, 318; Klason and Wanselin, *J. prakt. Chem.*, 1856, [2], 67, 41; Blomstrand, *Ber.*, 1871, 4, 51.
[7] Cahours and Gal, *loc. cit.*

insoluble in alcohol or ether.[1] If the foregoing β-modification of bistriethylphosphine dichloroplatinum in dry chloroform solution be treated with ammonia, an *ammino-compound* results, $(NH_3)_2Pt[P(C_2H_5)_3.Cl]_2$.[2] This is a deliquescent crystalline mass, very soluble in water. It readily loses ammonia, gives no precipitate with potassium chloroplatinate, but yields a phenyl mercaptide with phenyl mercaptan. Treatment of the ammine with 2 equivalents of triethylphosphine in chloroform gives a white precipitate of the compound $[(C_2H_5)_3P]_2Pt(NH_3Cl)_2$. With K_2PtCl_4 it forms $[(C_2H_5)_3P]_2Pt(NH_3Cl)_2.PtCl_2$, and reaction also takes place in this case with phenyl mercaptan.

Triethylphosphine reacts violently with *o*-xylylene bromide in chloroform solution, forming *o-xylene triethylphosphonium bromide*, $C_6H_4[CH_2.P(C_2H_5)_3.Br]_2$.[3] This crystallises from a mixture of alcohol and ether and melts at 250° to 250·5° C. ; it is soluble in chloroform, alcohol or water, insoluble in ether. The aqueous solution reacts with silver oxide to give a solution of the *free base*. This is readily decomposed, hydriodic acid yielding an *acid iodide*, $C_6H_4[CH_2.P(C_2H_5)_3.I]_2.2HI$, forming regular crystals melting indefinitely about 247° C. The *chloride* is difficult to crystallise. The following are also known : *aurichloride*, $C_6H_4[CH_2.P(C_2H_5)_3.AuCl_4]_2$, golden-yellow needles, M.pt. 163° C., and a *platinichloride*, $C_6H_4[CH_2.P(C_2H_5)_3.Cl]_2.PtCl_4$, darkening at 200° C. and melting indefinitely at 235° to 236° C. *Phenyl azide* and triethylphosphine in ether solution form an *addition product*, $C_6H_5N_3.(C_2H_5)_3P$.[4]

Tri-n-propylphosphine, $CH_3(CH_2)_2P$.—12 c.c. of phosphorus trichloride in 50 c.c. of ether are added to the solution obtained from 56 c.c. of *n*-propyl bromide and 15 grams of magnesium in 300 c.c. of ether. The yield of purified phosphine is 10 grams, the product boiling at 103·5° C. at 50 mm. or 187·5° C. at 760 mm. ; density 0·807 at 25° C. The *carbon disulphide addition compound* melts at 108° C., and the *mercurichloride* at 137° C.[5]

Tri-isopropylphosphine, $[(CH_3)_2CH]_3P$.—This phosphine is formed when di-*iso*propylphosphine and *iso*propyl iodide are heated together at 120° C.[6] It yields a crystalline *hydriodide*, $C_9H_{21}P.HI$, soluble in water, insoluble in ether.

Tri-n-butylphosphine, $CH_3(CH_2)_3P$.—A solution of 42 c.c. of *n*-butyl bromide in 100 c.c. of anhydrous ether containing a trace of iodine is added during three hours to 10 grams of magnesium turnings and 150 c.c. of ether contained in an apparatus through which hydrogen is passed during the preparation. The resulting solution is cooled to 0° C. and treated with 9 c.c. of phosphorus trichloride in 50 c.c. of ether, this mixture being added dropwise. The whole is then warmed for 30 minutes on the water-bath, cooled below 0° C. and cautiously treated with a solution of 50 grams of ammonium chloride in 250 c.c. of water. The ether layer is removed, dried over anhydrous sodium sulphate, the ether distilled off in an atmosphere of carbon dioxide and the residue fractionated. The phosphine is then redistilled under 50 mm. pressure. The yield is about 11 grams.[7]

[1] Cahours and Hofmann, *Annalen*, 1857, 104, 13. [2] Klason and Wanselin, *loc. cit.*
[3] Partheil and Gronover, *Ber.*, 1900, 33, 606.
[4] Staudinger and Meyer, *Helv. Chim. Acta*, 1919, [ii], 619.
[5] Davies, Pearse and Jones, *J. Chem. Soc.*, 1929, p. 1262.
[6] Hofmann, *Ber.*, 1873, 6, 295.
[7] Davies and Jones, *J. Chem. Soc.*, 1929, p. 33.

Tri-*n*-butylphosphine boils at 149·5° C. (corr.) at 50 mm. pressure and has a density of 0·8118 at 25° C. It is a colourless liquid having the characteristic phosphine odour. With alcohol, ether and benzene it is miscible in all proportions, but immiscible with water; its molecular weight in freezing benzene is normal. It is less readily oxidised than the lower tertiary phosphines. When boiled in a current of air it is converted into the oxide. It combines with *carbon disulphide* in cold absolute alcohol solution, the *addition product* melting at 65·5° C. (corr.). This latter product is completely dissociated in hot ether or alcohol solution. A *mercuric chloride addition compound* is known, but it forms only a plastic mass, difficult to purify. The phosphine combines with methyl and ethyl iodides, yielding alkyltri-*n*-butylphosphonium iodide.

Tri-isobutylphosphine, $[(CH_3)_2CH.CH_2]_3P$, occurs in a 12-gram yield when 14 c.c. of phosphorus trichloride are added to 94 c.c. of *iso*butyl bromide and 20 grams of magnesium in ether solution. The phosphine boils at 126° C. at 50 mm. pressure, and it combines with carbon disulphide to give highly unstable red crystals. The *mercurichloride* crystallises in plates from alcohol, M.pt. 191·5° C.[1] The *hydriodide* may be isolated by heating di-*iso*butylphosphine and *iso*butyl iodide together at 100° C., the salt decomposing on treatment with sodium hydroxide to give the phosphine.[2] Prepared by the latter method the base boils at 215° C.

Tri-n-amylphosphine, $(C_5H_{11})_3P$, is prepared by the interaction of 10·5 c.c. of phosphorus trichloride and the magnesium *n*-amyl bromide made from 78 c.c. of amyl bromide and 15 grams of magnesium.[3] The yield is about 9 grams; the phosphine boils at 185·5° C. at 50 mm. pressure and has a density 0·820 at 25° C. The *carbon disulphide addition product* melts at 55° C., but a crystalline mercurichloride or methiodide has not been obtained.

Tri-isoamylphosphine [or *Tri(γ-methylbutyl) phosphine*], $(C_5H_{11})_3P$. —Phosphorus trichloride (10·5 c.c.) is added to the Grignard reagent from 78 c.c. of *iso*amyl bromide and 15 grams of magnesium. The ether solution of the phosphine is dried and the ether distilled off in an atmosphere of carbon dioxide; in order to prevent oxidation of the phosphine, the residue is fractionally distilled in a vacuum, and all subsequent manipulations with the phosphine are carried out in an enclosure filled with carbon dioxide, without bringing the substance into contact with air. The yield is 9 grams, and the product boils at 131° C. at 11 mm.[4] It forms red needles with carbon disulphide, M.pt. 79·5° C.

Tri(dl-β-methylbutyl)phosphine, $(C_5H_{11})_3P$.—This phosphine is obtained only in poor yield when 10·5 c.c. of phosphorus trichloride are added to the Grignard reagent from 77 c.c. of *dl*-β-methylbutyl bromide and 15 grams of magnesium. The product boils at 113° to 117° C. at 10 mm.

Compounds of the Type $R_2R'P$.

Dimethylethylphosphine, $C_2H_5.P(CH_3)_2$.—The hydrochloride of this phosphine is formed when dimethyldiethylphosphonium chloride

[1] Davies, Pearse and Jones, *J. Chem. Soc.*, 1929, p. 1262.
[2] Hofmann, *loc. cit.*
[3] Davies, Pearse and Jones, *loc. cit.*
[4] Compare Hofmann, *loc. cit.*

is decomposed by heat and the distillate treated with sodium hydroxide. The phosphine boils at 83° to 85° C.[1]

Methyldiethylphosphine, $CH_3.P(C_2H_5)_2$, is isolated in the form of its hydrochloride when triethylmethylphosphonium chloride is decomposed above 300° C. : [2]

$$(C_2H_5)_3(CH_3)PCl = (CH_3)(C_2H_5)_2P.HCl + C_2H_4$$

It is a liquid, B.pt. 110° to 112° C.

Diethylpropylphosphine, $C_3H_7.P(C_2H_5)_2$, is obtained in a similar manner to the preceding compound by heating triethylpropylphosphonium chloride. It is a liquid, B.pt. 146° to 149° C.

Diethylisoamylphosphine, $C_5H_{11}.P(C_2H_5)_2$, occurs when triethyl*iso*amylphosphonium chloride is subjected to dry distillation. It is a colourless, slightly viscous liquid, B.pt. 185° to 187° C., which does not oxidise so readily as triethylphosphine, and has an odour resembling that of fusel oil. The *hydrochloride* formed in the foregoing decomposition boils at 270° to 271° C., is very deliquescent, and with sodium hydroxide yields the free phosphine.

Compounds of the Types R_3PO, R_3PS, R_3PSe.

Trimethylphosphine oxide, $(CH_3)_3PO$, may be obtained by several methods : (1) Trimethylphosphine is oxidised in air, this changing it to the oxide.[3] (2) It occurs when tetramethylphosphonium hydroxide is decomposed by heat.[4] (3) Magnesium methyl iodide in ether solution is treated with phosphorus oxychloride and the reaction mixture decomposed by hydrochloric acid.[5] It is a deliquescent, crystalline mass, M.pt. 137° to 138° C., B.pt. 214° to 215° C. It gives rise to the following double compounds : [6] *Trimethylphosphine oxide hydrogen ferrocyanide,* $2(CH_3)_3PO.H_4Fe(CN)_6$, consisting of small colourless needles, becoming green on exposure to light or moist air, very soluble in water, insoluble in cold alcohol ; *trimethylphosphine oxide hydrogen cobalticyanide,* $2(CH_3)_3PO.H_3Co(CN)_6.1{\cdot}5H_2O$, crystallising in glistening needles, becoming light green at about 200° C., soluble in warm water or alcohol ; *trimethylphosphine oxide hydrogen aurichloride,* $2(CH_3)_3PO.HAuCl_4$, crystallising from water or alcohol in yellow, flat, hexagonal plates, M.pt. 94·5° C. ; *trimethylphosphine oxide hydrogen dichromate,* $2(CH_3)_3PO.H_2Cr_2O_7$, crystallising from water or dilute nitric acid in bright red, hard, glistening prisms, darkening at 200° C. and commencing to fuse at 204° C. ; *trimethylphosphine oxide hydrogen bismuthic iodide,* $2(CH_3)_3PO.HBiI_4$, separating from warm dilute hydriodic acid in clusters of bright red, prismatic needles, decomposing on heating or treating with an excess of water ; *trimethylphosphine oxide hydrogen platinichloride,* $4(CH_3)_3PO.H_2PtCl_6$, crystallising from water in beautiful, red, pyramidal needles, M.pt. 126° C., insoluble in alcohol ; *trimethylphosphine oxide zinc iodide,* $2(CH_3)_3PO.ZnI_2$, forming small white prisms, M.pt. 168° C. In addition to the foregoing platinum compound a *platinichloride,* $3(CH_3)_3PO.$

[1] Collie, *Trans. Chem. Soc.*, 1888, 53, 720.
[2] Collie, *ibid.*, 1888, 53, 719.
[3] Cahours and Hofmann, *Annalen*, 1857, 104, 1.
[4] Cahours and Hofmann, *loc. cit.*; Collie, *Trans. Chem. Soc.*, 1888, 53, 636.
[5] Pickard and Kenyon, *Trans. Chem. Soc.*, 1906, 89, 262.
[6] Pickard and Kenyon, *loc. cit.*

$2HCl.PtCl_4.H_2O$, is known ; [1] it crystallises in orange plates and needles. The oxide also forms a number of *addition compounds with organic acids* : [2] *Camphoric acid* yields clear, hard crystals, $2(CH_3)_3PO.C_8H_{14}(CO_2H)_2$, M.pt. 91° to 93° C. ; *trichloracetic acid* gives small, colourless crystals, $(CH_3)_3PO.CCl_3CO_2H$, M.pt. 67° C.

Trimethylphosphine sulphide, $(CH_3)_3PS$.—An ether solution of trimethylphosphine is treated with flowers of sulphur ; [3] after a time the latter disappears, when the solvent is removed and the residue boiled with water, the sulphide separating as the solution cools. It forms four-sided prisms, M.pt. 105° C.

Trimethylphosphine selenide, $(CH_3)_3PSe$.—This is obtained on replacing the sulphur in the preceding preparation by selenium. The product forms prisms, M.pt. 84° C., which blacken on exposure to the air, selenium separating out.

Triethylphosphine oxide, $(C_2H_5)_3PO$, may be obtained by the following methods : (1) By the oxidation of triethylphosphine by air, nitric acid or mercuric oxide.[4] (2) By the action of potassium hydroxide on the product resulting from reaction between zinc diethyl and the compound $C_2H_5OPCl_2$.[5] (3) One part of white phosphorus and 13 parts of ethyl iodide are heated together for 24 hours at 175° to 180° C., and the reaction mass then boiled with 97 per cent. alcohol until no more ethyl iodide is formed. The solution is then distilled with 4 parts of potassium hydroxide.[6] (4) Magnesium ethyl bromide is allowed to react with phosphorus oxychloride and the mixture then decomposed with dilute hydrochloric acid.[7] (5) By heating the reaction product from zinc diethyl and phosphorus oxychloride with potassium hydroxide and a little water.[8]

The oxide forms colourless, odourless needles, M.pt. 51·9° C., B.pt. 242·8° to 243° C. It is slightly volatile in steam, and is more soluble in water and alcohol than in ether. It is precipitated from its aqueous solution by potassium hydroxide. It is indifferent to oxygen and ozone.[9] According to Cahours and Hofmann [10] it is reduced to triethylphosphine when warmed with sodium, but this is denied by Crafts and Silva.[11] When hydrochloric acid gas is passed into molten triethylphosphine oxide, a deliquescent mass results, to which the formula $(C_2H_5)_3PO.(C_2H_5)_3PCl_2$ is ascribed.[12] The following double compounds are known :[13] *Triethylphosphine oxide hydrogen ferrocyanide*, $2(C_2H_5)_3PO.H_4Fe(CN)_6$, a microcrystalline powder, quickly becoming green in moist air ; *triethylphosphine oxide hydrogen cobalticyanide*, $2(C_2H_5)_3PO.H_3Co(CN)_6.4H_2O$, forming white, prismatic crystals, M.pt. 174° C. ; *triethylphosphine oxide hydrogen aurichloride*, $2(C_2H_5)_3PO.HAuCl_4$, flat, yellow,

[1] Collie, *loc. cit.*
[2] Pickard and Kenyon, *loc. cit.*
[3] Cahours and Hofmann, *loc. cit.*
[4] Cahours and Hofmann, *loc. cit.*
[5] Wichelhaus, *Ber.*, 1868, 1, 77.
[6] Crafts and Silva, *Trans. Chem. Soc.*, 1871, 24, 629; *Jahresber.*, 1871, p. 764; see Carius, *Annalen*, 1866, 137, 118; Masson and Kirkland, *Trans. Chem. Soc.*, 1889, 55, 141.
[7] Pickard and Kenyon, *loc. cit.*
[8] Pebal, *Annalen*, 1861, 118, 22; 120, 198.
[9] Engler and Wild, *Ber.*, 1897, 30, 1673.
[10] Cahours and Hofmann, *loc. cit.*
[11] Crafts and Silva, *loc. cit.*
[12] Hofmann, *Annalen Suppl.*, 1861, 1, 19; *Phil. Trans.*, 1860, 150, 409. Compare Crafts and Silva, *Jahresber.*, 1871, p. 766.
[13] Pickard and Kenyon, *loc. cit.*

hexagonal plates, M.pt. 54° to 56° C.; *triethylphosphine oxide hydrogen dichromate*, $2(C_2H_5)_3PO.H_2Cr_2O_7$, forming hair-like needles, M.pt. 100° to 102° C.; *triethylphosphine oxide hydrogen bismuthic iodide*, $2(C_2H_5)_3PO.HBiI_4$, separating from dilute hydriodic acid as bright red, prismatic needles, decomposing above 130° C.; *triethylphosphine oxide hydrogen mercuric iodide*, $2(C_2H_5)_3PO.HHgI_3$, consisting of beautiful yellow needles sintering at 31° C. and melting at 32° to 33° C.; *triethylphosphine oxide hydrogen platinichloride*, $4(C_2H_5)_3PO.H_2PtCl_6$, M.pt. 150° C.; $3(C_2H_5)_3PO.(C_2H_5)_3PCl_2.PtCl_4$, monoclinic prisms;[1] *triethylphosphine oxide cupric chloride*, $(C_2H_5)_3PO.CuCl_2$,[2] pale brown prisms from alcohol, M.pt. 233° C., decomposed by water; *triethylphosphine oxide copper sulphate*, $2(C_2H_5)_3PO.CuSO_4$, green four-sided prisms;[3] *triethylphosphine oxide zinc iodide*, $2(C_2H_5)_3PO.ZnI_2$, forming monoclinic, prismatic crystals, M.pt. 99° C.[4] With *pyruvic acid* the oxide forms a *compound* $(C_2H_5)_3PO.2CH_3COCO_2H$, consisting of small, colourless, prismatic needles, M.pt. 75° to 77° C.

Triethylphosphine sulphide, $(C_2H_5)_3PS$, is best prepared from the phosphine as described for the corresponding methyl compound.[5] It may also be obtained by the interaction of triethylphosphine and ethyl mercaptan in the presence of air, or by boiling the compound $(C_2H_5)_3P(CS)S$ in alcohol with silver oxide or heating it at 100° C. with water. The sulphide forms hexagonal prisms, M.pt. 94° C., readily volatile in steam.[6] It forms a *compound with methyl iodide*, $(C_2H_5)_3PS.CH_3I$, consisting of colourless crystals, M.pt. 123° C., slowly decomposed by boiling water.[7] The methiodide is normally dissociated in aqueous solution and has almost the same conductivity as triethyl sulphonium iodide. The methiodide is decomposed by alkalis below 0° C., the *free base* decomposing immediately into mercaptan and triethylphosphine oxide.

Triethylphosphine selenide, $(C_2H_5)_3PSe$, occurs when selenium reacts with triethylphosphine in ether solution.[8] It may be crystallised from water, but is partially decomposed on contact with air. When dry the crystals are red and melt at 112° C.

Tri-n-propylphosphine oxide, $(C_3H_7)_3PO$.—A dilute ether solution of magnesium *n*-propyl bromide is well cooled and very slowly and with constant shaking mixed with a dry ether solution containing the calculated quantity of phosphorus oxychloride. After the vigorous reaction has subsided, the mass is decomposed with dilute hydrochloric acid, the ether removed and the residue mixed with a large excess of sodium hydroxide. The mixture is then distilled from a copper flask and the aqueous distillate fractionated, the oxide occurring in the fraction boiling at 260° to 265° C. at 759 mm. The freshly distilled oxide solidifies to colourless, lustrous, silky needles, M.pt. 38° C., which are odourless and very hygroscopic.[9] The oxide forms the following

[1] Hofmann, *loc. cit.*; Sella, *Annalen Suppl.*, 1861, 1, 17. Compare Groth, *Ch. Kr.*, 3, 44.
[2] Pickard and Kenyon, *loc. cit.*
[3] Pebal, *loc. cit.*
[4] Hofmann, *loc. cit.*; Sella, *loc. cit.*
[5] Cahours and Hofmann, *Annalen*, 1857, 104, 23; Hofmann, *Phil. Trans.*, 1860, 150, 409.
[6] See Sella, *loc. cit.*; Groth, *Ch. Kr.*, 3, 44.
[7] Hantzsch and Hibbert, *Ber.*, 1907, 40, 1508.
[8] Cahours and Hofmann, *loc. cit.*; Hofmann, *loc. cit.*
[9] Pickard and Kenyon, *loc. cit.*

double compounds: *Tri-n-propylphosphine oxide hydrogen ferrocyanide*, $2(C_3H_7)_3PO.H_4Fe(CN)_6$, colourless needles, sparingly soluble in water or alcohol; *tri-n-propylphosphine oxide hydrogen cobalticyanide*, $2(C_3H_7)_3PO.H_3Co(CN)_6.6H_2O$, pale yellow cubic crystals from water, M.pt. 119° C.; *tri-n-propylphosphine oxide hydrogen aurichloride*, $2(C_3H_7)_3PO.H_4AuCl_4$, yellow, flat, hexagonal plates, M.pt. 67° to 69° C.; *tri-n-propylphosphine oxide hydrogen dichromate*, $2(C_3H_7)_3PO.H_2Cr_2O_7$, melting with decomposition at 164° C.; *tri-n-propylphosphine oxide hydrogen mercuric iodide*, $2(C_3H_7)_3PO.HHgI$, forming yellow needles, M.pt. 52° to 54° C.; *tri-n-propylphosphine oxide hydrogen platinichloride*, $6(C_3H_7)_3PO.H_2PtCl_6$, separating in light brown flakes, M.pt. 92° to 93° C., very soluble in water.

Tri-n-butylphosphine oxide, $(C_4H_9)_3PO$.—10 c.c. of phosphorus oxychloride in 50 c.c. of ether are added to the Grignard reagent from 42 c.c. of *n*-butyl bromide and 10 grams of magnesium in 250 c.c. of ether. Ammonium chloride is then added and, when the ether layer is fractionally distilled under 760 mm. pressure, the oxide passes over at 300° C. and solidifies in the receiver. The oxide may also be prepared by boiling the phosphine in a current of air and oxidising it with warm 40 per cent. nitric acid. The product forms hygroscopic, colourless needles.

Tri-isoamylphosphine oxide, $(C_5H_{11})_3PO$, is formed when the phosphine is oxidised by air.[1] It is a crystalline product, M.pt. 60° to 65° C., soluble in alcohol.

Quaternary Phosphonium Compounds.

A number of methods used for preparing phosphonium compounds has already been indicated on p. 7. Some tetra-alkylphosphonium hydroxides may be produced by heating white phosphorus and the corresponding alcohol above 250° C. for a long period. The compound P_2Hg_3 reacts with alkyl iodides to form quaternary compounds, and the latter also occur when trialkylphosphines react with alkyl halides. There are also special methods of preparation applying only to individual derivatives. The iodides are converted into the hydroxides by treatment with moist silver oxide, and bromides, cyanides, carbonates, acetates, oxalates and sulphates are similarly obtained when the appropriate silver salt is used. Such salts also result when the hydroxides are treated with the corresponding acids.

The mixed quaternary phosphonium compounds are prepared as indicated by the following equations:

$$\begin{aligned} R_3P + R'X &= R_3R'PX \\ R_2R'P + R'X &= R_2R_2'PX \qquad (X = \text{halogen}) \\ RR'R''P + R'''X &= RR'R''R'''PX \end{aligned}$$

The phosphorus-nitrogen phosphonium compounds are formed when the phosphines containing nitrogen directly attached to phosphorus combine with alkyl iodides, *e.g.*

$$[(C_2H_5)_2N]_3P + CH_3I = [(C_2H_5)_2N]_3P(CH_3)I$$ [2]

[1] Hofmann, *Ber.*, 1873, 6, 303.

[2] It should be noted that these N-phosphines are not organometallic from the point of view of this volume until they form phosphonium compounds, for only in the latter case is the phosphorus directly linked to carbon.

The phosphonium iodides form addition products with the iodides of mercury, bismuth and thallium, and also with bismuth chloride. Perhalides, $R_4PI.X_2$, are formed when halogens react with the iodides, these products, like the original iodides, having well-defined crystalline forms ; moist silver oxide removes the iodine, giving the corresponding hydroxides. Like the arsonium chlorides the tetra-alkylphosphonium chlorides tend to be deliquescent, but they yield crystalline double salts with the chlorides of gold, mercury, platinum, bismuth and zinc. When two molecular equivalents of triethylphosphine react with one molecular equivalent of methylene chloride, ethylene dichloride or ethylene dibromide, phosphonium compounds result in which two atoms of phosphorus are present.

Tetramethylphosphonium hydroxide, $(CH_3)_4POH$.—When white phosphorus and methyl alcohol in the ratio 1 : 2 by weight are heated together in a sealed tube at a temperature not lower than 250° C. for several hours, the phosphorus disappears.[1] The phosphonium hydroxide is the main product of the reaction, the by-products consisting of phosphine, methylphosphine, and phosphinic and phosphoric acids. The hydroxide is also obtained when the corresponding phosphonium iodide is treated with moist silver oxide.[2] It reacts with acids, forming salts, and its conductivity has the value $\mu_\infty = 207$.[3] When decomposed by heat the hydroxide yields trimethylphosphine oxide and methane:[4]

$$(CH_3)_4P.OH \longrightarrow (CH_3)_3PO + CH_4$$

Most of the salts obtained from it are hygroscopic, but an exception is found in hydroxytrimethylphosphonium trichloroacetate, M.pt. 64° C.[5]

Tetramethylphosphonium iodide, $(CH_3)_4PI$, may be prepared in several ways : (1) By heating phosphonium iodide and methyl ether together in a sealed tube for six hours at 120° to 140° C.[6] (2) It forms the chief product when magnesium methyl iodide and phosphorus diiodide, P_2I_4, react in ether solution at the ordinary temperature and the resulting mass is decomposed by water.[7] (3) The *mercuric iodide addition product* of the iodide is formed when the compound P_2Hg_3 is heated for four hours with two parts of methyl iodide at 140° to 150° C.[8] (4) Tetramethylphosphonium hydroxide is converted to the iodide by treating it with hydriodic acid. (5) The iodide also occurs when trimethylphosphine reacts with methyl iodide.[9]

The iodide may be recrystallised from alcohol. It combines with iodine to yield a *periodide*, $(CH_3)_4PI.I_2$, a crystalline precipitate of the colour of chromic acid.[10] The *double salt with mercuric iodide*, $(CH_3)_4PI.2HgI_2$, forms yellow prisms, M.pt. 172° C., sparingly soluble in water,

[1] Berthaud, *Compt. rend.*, 1906, 143, 1166.
[2] Cahours and Hofmann, *Annalen*, 1857, 104, 31; Hofmann and Cahours, *Quart. J. Chem. Soc.*, 1859, 12, 56.
[3] Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 288.
[4] Cahours and Hofmann, *loc. cit.*; Collie, *Trans. Chem. Soc.*, 1888, 53, 636.
[5] Fenton and Ingold, *J. Chem. Soc.*, 1929, p. 2342.
[6] Fireman, *Ber.*, 1897, 30, 1088.
[7] Auger and Billy, *Compt. rend.*, 1904, 139, 597.
[8] Partheil and van Haaren, *Arch. Pharm.*, 1900, 238, 41.
[9] Cahours and Hofmann, *loc. cit.*
[10] Auger and Billy, *Compt. rend.*, 1904, 139, 639.

insoluble in ether.[1] Tetramethylphosphonium iodide is converted to the corresponding *picrate* when treated with aqueous sodium picrate; this crystallises in lemon-yellow needles which are unmelted at 290° C.[2]

Tetramethylphosphonium chloride, $(CH_3)_4PCl$, results when the hydroxide is treated with hydrochloric acid.[3] It is also obtained by the action of water on the reaction product from magnesium methyl iodide and phosphorus trichloride in ether solution at −20° C.[4] It is a deliquescent salt, which when strongly heated decomposes into ethylene and trimethylphosphonium chloride :[5]

$$2(CH_3)_4PCl = 2(CH_3)_3PHCl + C_2H_4$$

It forms a number of *double salts* : $(CH_3)_4PCl.AuCl_3$;[6] $(CH_3)_4PCl.HgCl_2$, crystallising from hot water in white needles, M.pt. 249° C., sparingly soluble in water, insoluble in ether ;[7] $2(CH_3)_4PCl.PtCl_4$, crystallising from water in octahedra, insoluble in alcohol or ether.[8]

Tetramethylphosphonium sulphate, $[(CH_3)_4P]_2SO_4$, occurs when the corresponding iodide is treated with silver sulphate.[9] The product crystallises in thick needles which decompose on strong heating with formation of trimethylphosphine oxide and trimethylphosphine sulphide.

Tetramethylphosphonium benzoate, $(CH_3)_4P.CO_2C_6H_5$, is prepared by neutralising the base with benzoic acid. It is a deliquescent substance, which decomposes above 300° C. into trimethylphosphine oxide and acetophenone :

$$(CH_3)_4P.CO_2C_6H_5 = (CH_3)_3PO + CH_3.CO.C_6H_5$$

Tetra-ethylphosphonium hydroxide, $(C_2H_5)_4POH$, may be obtained by the following methods : (1) White phosphorus and ethyl alcohol in the ratio 1 : 2 by weight are heated together for several hours at a temperature not lower than 250° C. The following by-products also occur: phosphine, ethyl phosphines, phosphinic acids and phosphoric acid.[10] (2) By heating a mixture of phosphonium iodide and diethyl ether in a sealed tube for six hours at 160° C.[11] (3) The corresponding iodide is treated with silver oxide in the presence of water and the filtered solution evaporated over sulphuric acid.[12] The base is obtained as a deliquescent, crystalline mass, which absorbs carbon dioxide from the air. The aqueous solution has a bitter taste and is strongly alkaline. When decomposed by distillation the hydroxide yields triethylphosphine oxide and ethane.[13] Acids convert the base into the corresponding salts.

Tetra-ethylphosphonium iodide, $(C_2H_5)_4PI$, can be obtained in several ways : (1) By the combination of triethylphosphine and ethyl iodide in ether solution.[14] The reaction takes place with violence in the cold and the whole solidifies to a white crystalline mass. (2) By

[1] Partheil and van Haaren, *loc. cit.*
[2] Fenton and Ingold, *loc. cit.*
[3] Cahours and Hofmann, *loc. cit.*
[4] Auger and Billy, *Compt. rend.*, 1904, **139**, 597.
[5] Collie, *loc. cit.*
[6] Cahours and Hofmann, *loc. cit.*
[7] Partheil and van Haaren, *loc. cit.*
[8] Cahours and Hofmann, *loc. cit.*
[9] Collie, *loc. cit.*
[10] Berthaud, *Compt. rend.*, 1906, **143**, 1166.
[11] Fireman, *Ber.*, 1897, **30**, 1088.
[12] Cahours and Hofmann, *Annalen*, 1857, **104**, 15; Letts and Collie, *Phil. Mag.*, 1886, [5], **22**, 183.
[13] Hofmann and Cahours, *Quart. J. Chem. Soc.*, 1859, **12**, 56; Letts and Collie, *loc. cit.*
[14] Cahours and Hofmann, *loc. cit.*; Hofmann and Cahours, *loc. cit.*; Letts and Collie, *loc. cit.*

heating one equivalent of phosphonium iodide with three equivalents of methyl alcohol for six to eight hours at 160° to 180° C. Triethylphosphonium iodide occurs as a by-product.[1] (3) Ethyl iodide and phosphorus in the ratio $7C_2H_5I$ to 2P are heated together in a sealed tube at 180° C. for about twenty-four hours.[2] When cold the product is black and is either a tarry liquid or a semi-solid crystalline mass of periodide. A little gas escapes when the tube is opened and excess of ethyl iodide is removed by distillation. The residue is mixed with water and treated with hydrogen sulphide, the clear solution being decanted from the precipitated sulphur and treated with silver oxide in excess to give the tetra-ethylphosphonium hydroxide. Instead of carrying out the last-mentioned stage of the process, the solution containing the hydrogen sulphide may be subjected to the action of a current of carbon dioxide to remove the former gas, then saturated with potassium hydroxide and warmed; the phosphonium iodide separates out and floats as an oily layer upon the potassium hydroxide solution. The reaction taking place in this preparation is represented as follows:

$$7C_2H_5I + 2P = (C_2H_5)_4PI_3 + (C_2H_5)_3PI_4$$

The decomposition of these polyiodides by the hydrogen sulphide occurs as follows:[3]

$$(C_2H_5)_4PI_3 + H_2S = (C_2H_5)_4PI + 2HI + S$$
$$(C_2H_5)_3PI_4 + H_2S + H_2O = (C_2H_5)_3PO + 4HI + S$$

(4) The iodide occurs as its double salt with zinc iodide when phosphorus, ethyl iodide and zinc are heated together at 160° C.,[4] or on heating ethyl iodide with a phosphorus-zinc alloy at 180° C.[5] (5) The double salt with mercuric iodide, $(C_2H_5)_4PI.2HgI_2$, is formed when the compound P_2Hg_3 is heated for four to five hours with about two parts of ethyl iodide at about 160° C.[6] (6) Heating zinc phosphide and ethyl iodide together in a sealed tube at 170° to 180° C. for twenty-four hours and treating the reaction mixture with potassium hydroxide gives the iodide.[7]

The iodide crystallises from a mixture of alcohol and ether in trigonal scalenohedral crystals,[8] readily soluble in water, sparingly soluble in alcohol, insoluble in ether. Its refractive index has been determined by Zecchini.[9] Aqueous potassium hydroxide does not affect the iodide. When treated with *chlorine* at about 70° C. the dry iodide yields a *compound*, $(C_2H_5)_4PI.Cl_4$; this slowly loses chlorine in dry air, and chlorine is evolved when the compound is treated with water or alcohol. Evaporation of the alcoholic solution gives an *iododichloride* having the composition, $(C_2H_5)_4PI.Cl_2$, which can be isolated in the form of yellow crystals.[10] When tetra-ethylphosphonium iodide is treated with bromine, much heat is developed, and if the free bromine be removed by evaporation and washing the residue with ether, a bright

[1] Hofmann, *Ber.*, 1871, 4, 205.
[2] Masson and Kirkland, *Trans. Chem. Soc.*, 1889, 55, 138.
[3] Compare Carius, *Annalen*, 1866, 137, 117; Crafts and Silva, *Jahresber.*, 1871, p. 764.
[4] Hofmann, *Annalen Suppl.*, 1861, 1, 4.
[5] Cahours, *Annalen*, 1862, 122, 331.
[6] Partheil and van Haaren, *Arch. Pharm.*, 1900, 238, 35.
[7] Cahours, *Annalen*, 1862, 122, 329.
[8] Groth, *Ch. Kr.*, 1, 197.
[9] Zecchini, *Gazzetta*, 1893, 23, i, 101.
[10] Masson and Kirkland, *Trans. Chem. Soc.*, 1889, 55, 126.

yellow solid results. This is dissolved in warm alcohol, when evaporation of the solution gives orange-red crystals having the composition $(C_2H_5)_4PI.Br_2$. This *iododibromide* is converted by ammonium hydroxide into a black explosive substance to which the formula $[(C_2H_5)_4PI.Br_2].2NH_3$ is assigned. In air the ammonia is slowly given off, leaving the iododibromide as a red powder. When two atomic equivalents of iodine in alcohol solution are added to a warm solution of the phosphonium iodide in the same solvent, brown glistening plates are deposited. The product is a *periodide*, $(C_2H_5)_4PI.I_2$, M.pt. 66° to 67° C., readily soluble in alcohol, less soluble in ether and insoluble in carbon disulphide.[1] Its brown solution is decolorised by reducing agents and gives easily soluble *double salts* when treated with *mercury halides*. The iodide also forms *double salts with bismuth halides*: $3(C_2H_5)_4PI.2BiCl_3$, golden-yellow crystals; $3(C_2H_5)_4PI.BiI_3$, brick-red crystals. With *mercuric iodide* it yields $2(C_2H_5)_4PI.HgI_2$, colourless plates from hot alcohol, M.pt. 202° C.; $(C_2H_5)_4PI.2HgI_2$, yellow needles from acetone-alcohol, M.pt. 117° C.[2] With *thallic iodide*, $(C_2H_5)_4PI.TlI_3$, scarlet needles, is formed, insoluble in water and sparingly soluble in cold alcohol.[3] Tetra-ethylphosphonium iodide and sodium triphenylmethyl react in ether solution to give triphenylmethane, triethylphosphine and sodium iodide.[4]

Tetra-ethylphosphonium chloride, $(C_2H_5)_4PCl$, can only be isolated as a deliquescent, crystalline mass.[5] It decomposes quantitatively above 300° C. into triethylphosphonium chloride, $(C_2H_5)_3PHCl$, and ethylene. The dry chloride absorbs chlorine at 105° to 110° C. and turns yellow, finally liquefying; the liquid on cooling deposits crystals of the *trichloride*, $(C_2H_5)_4PCl.Cl_2$,[6] a yellow, deliquescent substance, insoluble in ether, but decomposed by water or alcohol forming the chloride. For this preparation the chloride is prepared by shaking a solution of the phosphonium iodide with freshly precipitated silver chloride and drying the resulting product at 110° C. The following *double salts* have been obtained: $(C_2H_5)_4PCl.AuCl_3$, golden, glistening needles from water, M.pt. 179° C.;[7] $2(C_2H_5)_4PCl.ZnCl_2$, readily soluble in water;[8] $(C_2H_5)_4PCl.2HgCl_2$, white needles, M.pt. 130° C., readily dissolving in hot water or hot alcohol, but insoluble in ether;[9] $3(C_2H_5)_4PCl.2BiCl_3$, pale yellow crystals;[10] $2(C_2H_5)_4PCl.PtCl_4$, crystallising from water in octahedra, insoluble in alcohol or ether.[11]

Tetra-ethylphosphonium bromide, $(C_2H_5)_4PBr$, is prepared from the iodide by shaking its aqueous solution with silver bromide.[12] The dry salt absorbs bromine vapour at 110° C. to form a dark red liquid which at ordinary temperatures yields a scarlet, crystalline solid, $(C_2H_5)_4PBr.Br_6$. This is not stable in air, and solution in alcohol converts it into the tribromide, $(C_2H_5)_4PBr.Br_2$. The phosphonium

[1] Jörgensen, *J. prakt. Chem.*, 1871, [2], 3, 355.
[2] Partheil and van Haaren, *Arch. Pharm.*, 1900, 238, 35.
[3] Jörgensen, *J. prakt. Chem.*, 1872, [2] ,6, 87.
[4] Coffman and Marvel, *J. Amer. Chem. Soc.*, 1929, 51, 3496.
[5] Letts and Collie, *Phil. Mag.*, 1886, [5], 22, 201.
[6] Masson and Kirkland, *loc. cit.*
[7] Cahours and Hofmann, *Annalen*, 1857, 104, 18; Partheil and van Haaren, *loc. cit.*
[8] Pebal, *Annalen*, 1861, 120, 198.
[9] Partheil and van Haaren, *loc. cit.*
[10] Jörgensen, *loc. cit.*
[11] Cahours and Hofmann, *loc. cit.*
[12] Masson and Kirkland, *loc. cit.*

bromide yields a bright yellow *double salt with bismuth bromide*, $3(C_2H_5)_4PBr.BiBr_3$, which is comparable with the corresponding ammonium compound, $3(C_2H_5)_4NBr.BiBr_3$.[1]

Tetra-ethylphosphonium sulphate, $[(C_2H_5)_4P]_2SO_4$, occurs when the iodide is treated with silver sulphate. Dry distillation of the sulphate causes decomposition with formation of triethylphosphine oxide and sulphide.[2] Bromine vapour reacts with the dry sulphate at 110° C. yielding a red mass corresponding to $[(C_2H_5)_4P]_2SO_4.Br_{12}$.[3] Chlorine is absorbed less readily by the sulphate even at 130° C., yielding $[(C_2H_5)_4P]_2SO_4.Cl_4$, a yellow solid which dissolves in water with effervescence due to the evolution of chlorine; the compound deliquesces on exposure to the air and slowly loses chlorine in a current of dry air.

Tetra-ethylphosphonium nitrite, $(C_2H_5)_4PNO_2$, occurs when the sulphate is treated with barium nitrite. It is a pale yellow deliquescent product.[4]

Tetra-ethylphosphonium cyanide, $(C_2H_5)_4PCN$, is formed by the action of silver cyanide upon the phosphonium iodide.[5] When it is heated with water it is decomposed, forming triethylphosphine oxide, hydrocyanic acid and ethane.

Tetra-ethylphosphonium carbonate, $[(C_2H_5)_4P]_2CO_3$, forms highly deliquescent, needle-shaped crystals. These at 240° to 250° C. are decomposed with formation of triethylphosphine, triethylphosphine oxide, diethyl ketone, carbon dioxide and a gaseous hydrocarbon (C_4H_{10}?). An *acid carbonate* is known, and this gives a similar result when decomposed by heat.

Tetra-ethylphosphonium acetate, $(C_2H_5)_4P.OCOCH_3$, crystallises in needles which are highly deliquescent, and on heating is decomposed into triethylphosphine, triethylphosphine oxide, methyl ethyl ketone, methane, ethylene and carbon dioxide:

$$(C_2H_5)_4P.OCOCH_3 = (C_2H_5)_3PO + C_2H_5COCH_3$$
$$(C_2H_5)_4P.OCOCH_3 = (C_2H_5)_3P + CO_2 + C_2H_4 + CH_4$$

Tetra-ethylphosphonium oxalate, $[(C_2H_5)_4P]_2C_2O_4$.—This salt separates as fine crystals which decompose at 200° to 230° C. into triethylphosphine oxide, triethylphosphine, diethyl ketone, ethylene, carbon dioxide and carbon monoxide.

Tetra-ethylphosphonium benzoate, $(C_2H_5)_4P.OCOC_6H_5$, is isolated as radiating, deliquescent crystals, M.pt. 160° C., decomposed by heat into triethylphosphine, triethylphosphine oxide, phenyl ethyl ketone, ethyl benzoate, benzene, ethylene and carbon dioxide.

Tetra-n-propylphosphonium bromide, $(C_3H_7)_4PBr$, crystallises best from alcohol, and decomposes at 200° C.[6]

Tetra-isopropylphosphonium iodide, $[(CH_3)_2CH]_4PI$,[7] may be prepared by the interaction of tri-*iso*propylphosphine and *iso*propyl iodide at 100° C. It crystallises in cubes or octahedra.

Tetra-isobutylphosphonium iodide, $[(CH_3)_2.CH.CH_2]_4PI$.—This

[1] Jörgensen, *loc. cit.*
[2] Letts and Collie, *loc. cit.*
[3] Masson and Kirkland, *loc. cit.*
[4] C. Rây and N. Rây, *J. Indian Chem. Soc.*, 1928, 5, 733.
[5] Letts and Collie, *loc. cit.*
[6] Davies, Pearse and Jones, *J. Chem. Soc.*, 1929, p. 1262.
[7] Hofmann, *Ber.*, 1873, 6, 295.

product has not been obtained in the pure state. It is crystalline and is formed when tri-*iso*butylphosphine and *iso*butyl iodide are heated together for several hours at 120° C.

Tetra-isoamylphosphonium iodide, $(C_5H_{11})_4PI$, is a crystalline product resulting from the interaction of tri-*iso*amylphosphine and *iso*amyl iodide.

Mixed Quaternary Phosphonium Compounds.

Trimethylethylphosphonium iodide, $(CH_3)_3P(C_2H_5)I$, may be isolated: (1) By treating trimethylphosphine with ethyl iodide.[1] (2) By the interaction of dimethylethylphosphine and methyl iodide.[2] It separates in shining crystals from boiling alcohol.

Trimethylethylphosphonium chloride, $(CH_3)_3P(C_2H_5)Cl$, obtained in the usual manner from the iodide, is a deliquescent substance. When heated above 300° C. it decomposes without melting with formation of ethylene and trimethylphosphonium chloride or dimethylethylphosphonium chloride:

$$(CH_3)_3P(C_2H_5)Cl = (CH_3)_3PHCl + C_2H_4$$
$$2(CH_3)_3P(C_2H_5)Cl = 2(CH_3)_2P(C_2H_5)HCl + C_2H_4$$

The chloride yields a *platinichloride*, $2C_5H_{14}PCl.PtCl_4$, which crystallises from water in octahedra.

Trimethyl-β-bromoethylphosphonium bromide, $CH_2Br.CH_2.P(CH_3)_3Br$,[3] occurs when trimethylphosphine and an excess of ethylene dibromide are heated together in absolute alcohol at 50° to 60° C. The crystals are rhombic-bipyramidal.[4] It forms a *platinichloride*, $2C_5H_{13}Br.P.Cl.PtCl_4$, orange-yellow needles.

Trimethyl-β-hydroxyethylphosphonium chloride, $CH_2OH.CH_2.P(CH_3)_3Cl$.—This chloride is formed when a solution of trimethyl-β-bromoethylphosphonium chloride is treated with silver oxide and the filtered solution acidified with hydrochloric acid. The *platinichloride*, $2C_5H_{14}OPCl.PtCl_4$, crystallises in octahedra, readily soluble in water.

Trimethyl - carboxymethyl - phosphonium chloride, $(CH_3)_3P(CH_2.CO_2H)Cl$. — This is formed by the condensation of trimethylphosphine and monochloracetic acid.[5] It is a deliquescent, crystalline mass, yielding an orange-yellow, crystalline *platinichloride*, $2C_5H_{12}O_2PCl.PtCl_4$, readily soluble in boiling water. The phosphonium *iodide*, $C_5H_{12}O_2PI$, forms plates, easily soluble in water.

Trimethylisoamylphosphonium iodide, $C_5H_{11}.P(CH_3)_3I$, results when trimethylphosphine reacts with *iso*amyl iodide in ether solution.[6] It crystallises from alcohol in needles. The corresponding *chloride* yields a *platinichloride*, $2C_5H_{11}P(CH_3)_3Cl.PtCl_4$, consisting of orange-yellow needles, readily soluble in water.

Triethylmethylphosphonium iodide, $(C_2H_5)_3P(CH_3)I$.—Triethylphosphine and methyl iodide react with explosive violence, so that it is necessary to use ether as a solvent in preparing the phosphonium iodide. The methyl iodide may be replaced by methylene

[1] Cahours and Hofmann, *Annalen*, 1857, 104, 33.
[2] Collie, *Trans. Chem. Soc.*, 1888, 53, 720.
[3] Hofmann, *Annalen Suppl.*, 1861, 1, 282; *Phil. Trans.*, 1860, 150, 497.
[4] Sella, *Annalen Suppl.*, 1861, 1, 283; compare Groth, *Ch. Kr.*, 1, 194.
[5] Meyer, *Ber.*, 1871, 4, 736.
[6] Cahours and Hofmann, *loc. cit.*

iodide, using a large volume of ether at 100° C., but by-products result in this reaction.[1] The iodide is crystalline and yields the corresponding *hydroxide* when treated with moist silver oxide.[2]

Triethylmethylphosphonium chloride, $(C_2H_5)_3P(CH_3)Cl$.—The foregoing hydroxide yields the chloride when mixed with hydrochloric acid. The chloride gives a *platinichloride*, $2(C_2H_5)_3P(CH_3)Cl.PtCl_4$, consisting of shining octahedral crystals, insoluble in alcohol or ether, but crystallisable from boiling water.[3] Distillation of the chloride gives ethylene and a crystalline distillate which is converted by sodium hydroxide into methyldiethylphosphine.[4]

Triethyl-β-chloroethylphosphonium chloride, $CH_2Cl.CH_2.P(C_2H_5)_3Cl$,[5] occurs when triethylphosphine reacts with a large excess of ethylene dichloride in the cold. It crystallises in needles and forms a *platinichloride*, $2CH_2Cl.CH_2.P(C_2H_5)_3Cl.PtCl_4$, separating in orange-yellow needles. It is converted to the *β-hydroxyethyl compound* by moist silver oxide.

Triethyl-β-bromoethylphosphonium bromide, $CH_2Br.CH_2.P(C_2H_5)_3Br$.—The preparation of this compound is similar to that of the preceding chloride, the ethylene dichloride being replaced by ethylene dibromide. It crystallises from absolute alcohol-ether in cubic crystals, decomposing at about 235° C.[6] Silver chloride converts it into *triethyl-β-bromoethylphosphonium chloride*, and in a similar manner the *sulphate* and *nitrate* are obtained. Moist silver oxide replaces the bromine by *hydroxyl* groups, and heating with silver acetate and water at 100° C. transforms the bromide into *triethylvinylphosphonium acetate*. Alcoholic potassium hydroxide decomposes the bromide, and zinc and sulphuric acid reduce it to tetraethylphosphonium bromide. On heating at 100° C. for thirty minutes with alcoholic ammonia, the *hydrobromide* of *triethyl-β-aminoethylphosphonium bromide* is formed, whilst *trimethylphosphine* and *triethylarsine* give the following *compounds* respectively: $BrP(CH_3)_3.CH_2.CH_2.P(C_2H_5)_3Br$ and $BrP(C_2H_5)_3.CH_2.CH_2.As(C_2H_5)_3Br$.

Triethyl-β-bromoethylphosphonium iodide, $CH_2Br.CH_2.P(C_2H_5)_3I$, forms scales, sparingly soluble in cold water, whilst the corresponding *sulphate* crystallises in needles, very soluble in water or alcohol.

Triethyl-β-bromoethylphosphonium chloride, $CH_2Br.CH_2.P(C_2H_5)_3Cl$, is obtained as already described. It forms a *double salt* with *auric chloride*, $C_8H_{19}BrPCl.AuCl_3$, crystallising in pale yellow needles, sparingly soluble in cold water. The *platinichloride*, $2C_8H_{19}BrPCl.PtCl_4$, consists of orange-yellow, monoclinic prisms,[7] readily soluble in hot water but sparingly soluble in cold water.

Triethyl-β-hydroxyethylphosphonium hydroxide, $CH_2OH.CH_2.P(C_2H_5)_3OH$, is prepared by treating triethyl-β-bromoethylphosphonium bromide with silver oxide in the presence of water.[8] It is a

[1] Hofmann, *Jahresber.*, 1860, p. 342.

[2] Cahours and Hofmann, *loc. cit.*; Hofmann and Cahours, *Quart. J. Chem. Soc.*, 1859, **12**, 56.

[3] See Groth, *Ch. Kr.*, **1**, 479.

[4] Collie, *loc. cit.*

[5] Hofmann, *Annalen Suppl.*, 1861, **1**, 276; *Phil. Trans.*, 1860, **150**, 497.

[6] Sella, *Annalen Suppl.*, 1861, **1**, 156; compare Groth, *Ch. Kr.*, **1**, 197; Hofmann, *Annalen Suppl.*, 1861, **1**, 155.

[7] Sella, *loc. cit.*

[8] Hofmann, *Annalen Suppl.*, 1861, **1**, 164, 165.

white, hygroscopic mass, which has a strongly alkaline reaction. It decomposes on heating into triethylphosphine oxide and ethylene.

Triethyl-β-hydroxyethylphosphonium chloride, $CH_2OH.CH_2.P(C_2H_5)_3Cl$.—Molecular quantities of ethylene chlorhydrin and triethylphosphine condense to give this chloride when heated together for two hours at 150° C. in a sealed tube filled with carbon dioxide.[1] The product is a white, very hygroscopic crystalline mass, combining with *auric chloride* to form $C_8H_{20}OPCl.AuCl_3$, which crystallises from hot water. It melts at 171° to 172° C., and liquefies when heated under water. *Mercuric chloride* forms the *double salt* $C_8H_{20}OPCl.HgCl_2$, M.pt. 164° C. when crystallised from water. The *platinichloride*, $2C_8H_{20}OPCl.PtCl_4$, forms orange-yellow octahedra from water, M.pt. 221° to 222° C., belonging to the regular system.[2] *Triethyl-β-hydroxyethylphosphonium iodide* crystallises in needles, very soluble in water or alcohol.[3]

Triethyl-carboxymethyl-phosphonium chloride, $(C_2H_5)_3P(CH_2.CO_2H)Cl$, is formed when triethyl-carbethoxymethyl-phosphonium chloride is treated with silver oxide and the *anhydride* thus produced, $(C_2H_5)_3P<\begin{matrix}CH_2\\ \\ O\end{matrix}>CO$, is mixed with hydrochloric acid.[4] It yields a *platinichloride*, $2C_8H_{18}O_2PCl.PtCl_4$.

Triethyl-carbethoxymethyl-phosphonium chloride, $(C_2H_5)_3P(CH_2.CO_2C_2H_5)Cl$, is the condensation product of monochloracetic ester and triethylphosphine. It has only been isolated as a viscous mass.

Triethyl-β-aminoethylphosphonium bromide, $BrP(C_2H_5)_3.CH_2.CH_2NH_2$.—The bromine of the corresponding β-bromoethyl compound is replaced by the amino-group by heating with alcoholic ammonia at 100° C. for thirty minutes.[5] Treatment with moist silver oxide gives the *free base* as an oil, which is transformed into *triethyl-vinylphosphonium hydroxide* when heated.

Triethyl-β-aminoethylphosphonium chloride, $ClP(C_2H_5)_3.CH_2.CH_2.NH_2$, is prepared by the usual methods. It forms a *compound* with *auric chloride*, $C_8H_{21}NPCl.HCl.2AuCl_3$, golden-yellow needles, sparingly soluble in water, and with *platinic chloride*, $C_8H_{21}NPCl.HCl.PtCl_4$, yellow rhombic crystals,[6] sparingly soluble in boiling water.

Triethyl-β-methylaminoethylphosphonium bromide, $BrP(C_2H_5)_3.CH_2.CH_2.NHCH_3$, occurs as the *hydrobromide* when triethyl-β-bromoethylphosphonium bromide is heated with *methylamine* as described already for the β-amino-compound. The bromide is converted into the *hydroxide* by silver oxide in the presence of water, and the base with hydrochloric acid yields the *chloride*. The latter forms a *platinichloride*, $C_9H_{23}NPCl.HCl.PtCl_4$, crystallising in needles and sparingly soluble in water.

Ethylene-trimethylammonium hydroxide triethylphosphonium hydroxide, $HO.P(C_2H_5)_3.CH_2.CH_2.N(CH_3)_3OH$, is formed as *bromide hydrobromide* when the methylamine in the preceding preparation is replaced by triethylamine. The *base* may be isolated in

[1] Partheil and Gronover, *Arch. Pharm.*, 1903, **241**, 409.
[2] Sella, *loc. cit.*
[3] Hofmann, *loc. cit.*
[4] Hofmann, *Jahresber.*, 1862, p. 334.
[5] Hofmann, *Annalen Suppl.*, 1861, **1**, 290; *Phil. Trans.*, 1860, **150**, 497.
[6] See Groth, *Ch. Kr.*, **3**, 59.

the usual manner. The *chloride* yields a *platinichloride*, $C_{11}H_{28}NPCl_2.PtCl_4$, crystallising in needles.

Triethyl - β - ethylaminoethylphosphonium bromide, $BrP(C_2H_5)_3.CH_2.CH_2.NHC_2H_5$.—This is produced when ethylamine is used in the foregoing condensation. The solution of the *base* yields the *chloride* with hydrochloric acid, and the chloride forms a *platinichloride*, $C_{10}H_{25}NPCl.HCl.PtCl_4$, which crystallises from water in orange-yellow crystals.

Triethyl - β - diethylaminoethylphosphonium bromide, $BrP(C_2H_5)_3.CH_2.CH_2.N(C_2H_5)_2$, is isolated by using diethylamine in the foregoing condensation. It forms a *base*, the *chloride* of which gives a *platinichloride*, $C_{12}H_{29}NPCl.HCl.PtCl_4$, crystallising in plates.

Triethylhydroxymethylphosphonium iodide, $(C_2H_5)_3P(CH_2OH)I$, is the product of the interaction of methylene iodide and triethylphosphine, the reaction being carried out at 100° C. in ether solution.[1] The *base* may be isolated in the usual manner.

Triethylchloromethylphosphonium chloride, $(C_2H_5)_3P(CH_2Cl)Cl$.—Equimolecular quantities of methylene chloride and triethylphosphine are heated together at 100° C.[2] The chloride also occurs when chloromethenyl-*tris*-triethylphosphonium chloride (see below) is partially decomposed in aqueous solution.[3] It yields a *platinichloride*, $2C_7H_{17}ClPCl.PtCl_4$, crystallising in needles, sparingly soluble in water.

Triethyliodomethylphosphonium iodide, $(C_2H_5)_3P(CH_2I)I$.—In the preparation of this compound the methylene chloride in the foregoing is replaced by methylene iodide. The iodide crystallises from alcohol, and is readily soluble in water, insoluble in ether.[4] The *base*, obtained by the action of moist silver oxide, is converted to the *chloride* by hydrochloric acid. The chloride gives a *platinichloride*, $2C_7H_{17}IPCl.PtCl_4$, separating from boiling water as sparingly soluble needles.

Methenyl-tris-triethylphosphonium iodide, $[(C_2H_5)_3PI]_3CH$, is the condensation product of iodoform and triethylphosphine.[5] It is decomposed by moist silver oxide, forming triethylphosphine oxide and methyltriethylphosphonium hydroxide. It crystallises from alcohol, in which it is sparingly soluble, is readily soluble in water, insoluble in ether. A *zinc iodide double salt* is known, $2[(C_2H_5)_3PI]_3CH.ZnI_2$, a crystalline solid, sparingly soluble in water. The *chloride* forms a *platinichloride*, $2[(C_2H_5)_3PCl]_3CH.PtCl_4$, yellow monoclinic prisms from hot hydrochloric acid, sparingly soluble in water.[6]

Chloromethenyl - tris - triethylphosphonium chloride, $[(C_2H_5)_3PCl]_3CCl$.—Triethylphosphine and tetrachloromethane react in ether solution to give this chloride as a very hygroscopic mass.[7] Its aqueous solution partially decomposes with formation of triethylchloromethylphosphonium chloride. It forms a *platinichloride*, $2[(C_2H_5)_3PCl]_3CCl.3PtCl_4$. Replacement of tetrachloromethane by tetrabromomethane yields *bromomethenyl-tris-triethylphosphonium bromide.*

Triethyl-n-propylphosphonium chloride, $C_3H_7.P(C_2H_5)_3Cl$, is

[1] Hofmann, *Jahresber.*, 1860, p. 342.
[2] Hofmann, *ibid.*, 1861, p. 487.
[3] Hantzsch and Hibbert, *Ber.*, 1907, 40, 1516.
[4] Hofmann, *Jahresber.*, 1860, p. 341.
[5] Hofmann, *ibid.*, 1859, 377.
[6] Compare Groth, *Ch. Kr.*, 3, 44.
[7] Hantzsch and Hibbert, *loc. cit.*

prepared from triethylphosphine and propyl chloride by heating them together at 130° C.[1] It is decomposed by heat into ethylene and diethylpropylphosphine. It forms a *platinichloride*, $2C_9H_{22}PCl.PtCl_4$.

Triethylisoamylphosphonium iodide, $C_5H_{11}.P(C_2H_5)_3I$, is prepared from its components in the usual manner.[2] The reaction takes several days to complete in the cold and the iodide separates from the ether solution in shining crystals. The corresponding *chloride* is formed by heating an excess of *iso*amyl chloride with triethylphosphine at 130° C. ; it is deliquescent and difficult to crystallise ; [3] heat decomposes it into ethylene and diethyl*iso*amylphosphine. The chloride forms a *platinichloride*, $2C_5H_{11}.P(C_2H_5)_3Cl.PtCl_4$, crystallising in prisms, somewhat soluble in water but sparingly soluble in alcohol.

Triethylvinylphosphonium bromide, $CH_2{:}CH.P(C_2H_5)_3Br$.—This compound is obtained when triethyl-β-bromoethylphosphonium bromide is heated at 200° C.[4] The corresponding *hydroxide* occurs when a concentrated solution of triethyl-β-hydroxyethylphosphonium hydroxide is evaporated over a naked flame ; it may also be prepared by heating ethylene-*bis*-triethylphosphonium hydroxide at 200° C. or by heating triethyl-β-aminoethylphosphonium hydroxide. The *chloride* yields a *platinichloride*, $2C_8H_{18}PCl.PtCl_4$, crystallising in octahedra. An *acetate* may be isolated by heating triethyl-β-bromoethylphosphonium bromide with silver acetate and water at 100° C.

Triethylallylphosphonium iodide, $CH_2{:}CH.CH_2.P(C_2H_5)_3I$, is the condensation product of allyl iodide and triethylphosphine. It crystallises from alcohol in needles.[5]

Tri-n-propylmethylphosphonium iodide, $(C_3H_7)_3(CH_3)PI$, prepared from tri-*n*-propylphosphine and methyl iodide, melts at 212·5° C.[6]

Tri-n-butylmethylphosphonium iodide, $(C_4H_9)_3(CH_3)PI$, owing to the violence of the direct action between methyl iodide and the phosphine, is most conveniently prepared by mixing dilute ether solutions of the reactants ; the white crystalline precipitate, M.pt. 133·5° C., is purified by washing with ether.[7]

Tri-n-butylethylphosphonium iodide, $(C_4H_9)_3(C_2H_5)PI$, melts at 153° C.

Tri-isoamylmethylphosphonium iodide, $(C_5H_{11})_3(CH_3)PI$, is precipitated as an oil which solidifies on keeping.[8]

Dimethyldiethylphosphonium iodide, $(CH_3)_2P(C_2H_5)_2I$, is obtained by treating methyldiethylphosphine with methyl iodide.[9] The corresponding *chloride* decomposes when heated into ethylene and a distillate which yields dimethylethylphosphine when treated with sodium hydroxide. The *chloride* forms a *platinichloride*, $2C_6H_{16}PCl.PtCl_4$.

Methylethylisopropylisobutylphosphonium iodide, $(CH_3)_2CH.CH_2.P(CH_3)(C_2H_5)[CH(CH_3)_2]I$, is a crystalline compound, isolated

[1] Collie, *Trans. Chem. Soc.*, 1888, 53, 720.

[2] Cahours and Hofmann, *Annalen*, 1857, 104, 27; Hofmann and Cahours, *Quart. J. Chem. Soc.*, 1859, 12, 56.

[3] Collie, *loc. cit.*

[4] Hofmann, *Annalen Suppl.*, 1861, 1, 174; *Jahresber.*, 1860, p. 338; *Phil. Trans.*, 1860, 150, 449.

[5] Hofmann, *Annalen Suppl.*, 1861, 1, 52.

[6] Davies, Pearse and Jones, *J. Chem. Soc.*, 1929, p. 1262.

[7] Davies and Jones, *J. Chem. Soc.*, 1929, p. 33.

[8] Davies, Pearse and Jones, *loc. cit.*

[9] Collie, *loc. cit.*

from the interaction of ethyl*iso*propyl*iso*butylphosphine with methyl iodide.[1]

Methyltri-isobutylphosphonium iodide, $[(CH_3)_2CH.CH_2]_3P(CH_3)I$, is the condensation product of tri*iso*butylphosphine and methyl iodide; it may be recrystallised from water.

Nitrogen-Phosphorus Phosphonium Compounds.

Triethylamine-N-methylphosphonium iodide,[2] $[(C_2H_5)_2N]_3P(CH_3)I$, is a colourless oil, soluble in water, insoluble in ether.

Diethylamine - N - ethoxymethylphosphonium iodide, $[(C_2H_5)_2N]_2P(OC_2H_5)(CH_3)I$, is an oil, boiling at 145° to 148° C. at 22 mm.

Tri - n - propylamine - N - methylphosphonium iodide, $[(C_3H_7)_2N]_3P(CH_3)I$, forms white needles, M.pt. 83° to 84° C., readily soluble in water or alcohol.

Tri - isopropylamine - N - methylphosphonium iodide, $[(C_3H_7)_2N]_3P(CH_3)I$, yields white needles, M.pt. 138° C.

Di-sec.-propylamine-N-ethoxymethylphosphonium iodide, $[(C_3H_7)_2N]_2P(OC_2H_5)(CH_3)I$, is readily soluble in water and may be converted into the *dipropylamide* of methylphosphinic acid, $CH_3.PO[N(C_3H_7)_2]_2$, boiling at 176° to 180° C. at 25 mm.

Di - isobutylamine - dipiperidine - N - methylphosphonium iodide, $[(C_4H_9)_2N]_2P(C_5H_{10}N)_2(CH_3)I$, is an oil.

Di-isobutylamine-N-phenoxymethylphosphonium iodide, $[(C_4H_9)_2N]_2P(OC_6H_5)(CH_3)I$, crystallises in needles, M.pt. 132° C., soluble in alcohol, insoluble in ether.

Phosphonium Compounds containing Two Atoms of Phosphorus.

Methylene-bis-triethylphosphonium chloride or **Methylene-hexaethyldiphosphonium dichloride,** $Cl(C_2H_5)_3P.CH_2.P(C_2H_5)_3Cl$,[3] occurs when two molecular proportions of triethylphosphine react with one molecular proportion of methylene chloride. The product is a crystalline mass, decomposed by water with formation of methyltriethylphosphonium chloride, triethylphosphine oxide and hydrochloric acid.

Ethylene-bis-trimethylphosphonium bromide, $BrP(CH_3)_3.CH_2.CH_2.P(CH_3)_3Br$.—To produce this bromide, ethylene dibromide is heated with an excess of trimethylphosphine.[4] Its crystals are monoclinic-prismatic [5] and are very deliquescent. The corresponding *chloride* gives a *platinichloride*, $C_8H_{22}P_2Cl_2.PtCl_4$, golden yellow plates from boiling hydrochloric acid, insoluble in water. The *iodide* forms sparingly soluble needles.

Ethylene-trimethylphosphonium hydroxide triethylphosphonium hydroxide, $HO.P(CH_3)_3.CH_2.CH_2.P(C_2H_5)_3OH$.—This base is obtained by treating the corresponding dibromide with silver oxide in the presence of water. The *dibromide* is the product of the interaction of trimethylphosphine and triethyl-β-bromoethylphosphonium

[1] Hofmann, *Ber.*, 1873, 6, 301.
[2] Michaelis and Möttek, *Annalen*, 1903, 326, 163.
[3] Hofmann, *Jahresber.*, 1861, p. 487.
[4] Hofmann, *Annalen Suppl.*, 1861, 1, 287; *Jahresber.*, 1860, p. 340.
[5] Sella, *Annalen Suppl.*, 1861, 1, 288; see Groth, *Ch. Kr.*, 3, 58.

bromide. The *dichloride* forms a *platinichloride*, $C_{11}H_{28}P_2Cl_2.PtCl_4$, crystallising from boiling water in pale yellow scales.

Ethylene-bis-triethylphosphonium bromide, $BrP(C_2H_5)_3.CH_2.CH_2.P(C_2H_5)_3Br$, is obtained by the interaction of two molecular equivalents of triethylphosphine and one molecular equivalent of ethylene dibromide in ether solution. It crystallises in needles, readily soluble in absolute alcohol, insoluble in ether.[1] An aqueous solution of the *base* is formed by treating the bromide in water with silver oxide; evaporation yields a thick syrup which absorbs carbon dioxide from the air. When decomposed by heat above 160° C. the base yields triethylphosphine, triethylphosphine oxide and ethylene. The bromide forms an *addition product* with *silver bromide*.

Ethylene-bis-triethylphosphonium chloride, $ClP(C_2H_5)_3.CH_2.CH_2.P(C_2H_5)_3Cl$, is isolated when triethylphosphine and ethylene dichloride are heated together at 120° C. It forms highly deliquescent plates, soluble in water or alcohol. It yields the following *double salts*: $C_{14}H_{34}P_2Cl_2.2AuCl_3$, yellow needles, readily soluble in boiling water, sparingly in cold water; $2C_{14}H_{34}P_2Cl_2.3HgCl_2$, needles or plates, sparingly soluble in water or alcohol; $C_{14}H_{34}P_2Cl_2.PtCl_4$, orange-red monoclinic crystals from hydrochloric acid, insoluble in boiling water.[2]

Ethylene-bis-triethylphosphonium iodide, $IP(C_2H_5)_3.CH_2.CH_2.P(C_2H_5)_3I$, crystallises from boiling water in needles, M.pt. 231° C., readily soluble in hot water, sparingly soluble in alcohol and insoluble in ether; 100 parts of water at 100° C. dissolve 458·3 parts of the iodide; at 12° C. only 3·08 parts of the salt dissolve. The *double salt* with *zinc iodide*, $C_{14}H_{34}P_2I_2.ZnI_2$, crystallises from hot water in long needles.

Compounds Derived from the Action of Hydrogen Phosphide on Formaldehyde.

Tetrahydroxytetramethylphosphonium chloride,[3] $(CH_2OH)_4PCl$, is formed when hydrogen phosphide is passed into a warm aqueous solution of formaldehyde acidified with hydrochloric acid. It melts at 151° C., and with alkali hydroxides or carbonates reaction takes place in two stages, hydrogen (1 mol.) and formaldehyde (1 mol.) being liberated at each stage. Sodium hydroxide or carbonate below 80° C. and barium carbonate at 100° C. give *trihydroxytrimethylphosphine oxide*, the *tribenzoate* of which melts at 110° C.

Dihydroxydimethylphosphinic acid,[4] $(CH_2OH)_2PO(OH)$, is isolated in the form of its *barium salt* when the foregoing phosphonium chloride is boiled with aqueous barium hydroxide solution until evolution of hydrogen ceases. The salt forms well-developed crystals, moderately soluble in water, insoluble in alcohol.

Tetrachlorotetramethylphosphonium chloride, $(CH_2Cl)_4PCl$.—Tetrahydroxytetramethylphosphonium chloride and phosphorus pentachloride react when boiled together for four hours in carbon tetrachloride solution to give the tetrachloro-compound. It consists of white crystals, M.pt. 192° to 193° C., readily soluble in water, but not hygroscopic. In alcohol it is readily soluble, sparingly soluble in ethyl acetate, chloroform and carbon tetrachloride. The dry compound is

[1] Hofmann, *Annalen Suppl.*, 1861, 1, 177; *Phil. Trans.*, 1860, 150, 449.
[2] See Sella, *Annalen Suppl.*, 1861, 1, 197.
[3] Hoffman, *J. Amer. Chem. Soc.*, 1921, 43, 1684.
[4] Hoffman, *ibid.*, 1930, 52, 2995.

odourless, but the aqueous solution has a distinct odour due to hydrolysis and breaking up of the phosphonium hydroxide into the phosphine.

Trichlorotrimethylphosphine, $(CH_2Cl)_3P$, occurs when the preceding compound is hydrolysed by alkalis or sodium hydrogen carbonate. It boils at 100° C. at 7 mm., density 1·414 at 20° C. It is stable in air but is oxidised by nitric acid (density 1·2) to *trichlorotrimethylphosphine oxide*, $(CH_2Cl)_3PO$, M.pt. 78° C., a *hydrate* containing 0·5 mol. of water melting at 88° to 89° C. This oxide with sodium benzoate at 200° C. gives tribenzoyloxytrimethylphosphine oxide.

Compounds of the Type $RPCl_2$.

These compounds are best obtained by heating a mixture of mercury dialkyl and phosphorus trichloride in a sealed tube for six hours at 250°C. The compounds are clear mobile liquids of sharp, unpleasant odour, decomposed by water and coloured yellow in the presence of moisture.[1] The reaction takes the following course, but if a higher temperature than that stated above is used, the alkylmercuric halides formed in the reaction are decomposed :

$$R_2Hg + PCl_3 = RHgCl + RPCl_2$$

The following derivatives have been isolated : *Ethyldichlorophosphine*, B.pt. 114° to 117° C., density 1·2952 at 19° C. ; *n-propyldichlorophosphine*, B.pt. 140° to 143° C., density 1·1771 at 19° C. ; *isopropyldichlorophosphine*, B.pt. 135° to 138° C., density 1·2181 at 23° C. ; *isobutyldichlorophosphine*, B.pt. 155° to 157° C., density 1·1236 at 23° C. ; *isoamyldichlorophosphine*, B.pt. 180° to 183° C., density 1·1024 at 23° C.

When the foregoing compounds are treated with chlorine, they yield *tetrachlorides* of the type $RPCl_4$. These are yellowish-white substances resembling phosphorus pentachloride in appearance and rapidly changing to oxychlorophosphines in the air. They form *double compounds* with *inorganic halides*, *e.g.* $SbCl_5$ gives $RPCl_4.SbCl_5$. Bromine vapour yields white hygroscopic solids of the type $RPCl_2Br_2$. Sulphur dioxide converts the tetrachlorides into oxychlorides of the type $RPOCl_2$, and these derivatives are dealt with in the section on phosphinic acids. The alkyldichlorophosphines, when heated in a sealed tube for two to three hours with sulphur at 120° to 125° C. yield transparent, yellow liquids of pungent odour, which are stable in the presence of water and have the general formula $RPSCl_2$; the following compounds are known : *ethylthiodichlorophosphine*, B.pt. 80° to 82° C. at 50 mm., density 1·3606 at 70° C. ; *n-propylthiodichlorophosphine*, B.pt. 95° to 98° C. at 50 mm., density 1·2854 at 20° C. ; *isobutylthiodichlorophosphine*, B.pt. 110° to 113° C. at 50 mm., density 1·2515 at 20° C. ; *isoamylthiodichlorophosphine*, B.pt. 130° to 132° C. at 50 mm., density 1·1771 at 20 mm.

Compounds of the Type $RP(OH)_2$.

The following alkylphosphinous acids of the general formula $RP(OH)_2$ are obtained by the action of water on the corresponding alkyldichlorophosphines. They are colourless syrups, solidifying below 0° C., moderately soluble in water. They are monobasic and are some-

[1] Guichard, *Ber.*, 1899, **32**, 1572; compare Michaelis, *Ber.*, 1880, **13**, 2174.

times given the alternative structure $O=PH(R)OH$.[1] The densities of the known acids are as follows: *ethylphosphinous acid*, 1·2952 at 19° C.; *n-propylphosphinous acid*, 1·1418 at 13° C.; *isopropylphosphinous acid*, 1·1891 at 19° C.; *isobutylphosphinous acid*, 1·0740 at 23° C.; *isoamylphosphinous acid*, 1·0613 at 23° C. The alkali salts of the acids readily dissolve in water, but the alkaline earth, lead and iron salts are insoluble. The ethyl-acid is decomposed by heat into ethylphosphine and ethylphosphinic acid, and at 60° to 135° C. the *iso*amyl-acid yields *iso*amylphosphine and *iso*amylphosphinic acid. The *ammonium salt* of the *isoamyl-acid* crystallises in fine needles, readily soluble in water or alcohol; the *iron salt* is a white precipitate.

Compounds of the Type $RPO(OH)_2$.

These acids may be obtained in several ways:

(1) Pure primary phosphines are oxidised directly by fuming nitric acid.

(2) The corresponding alkylphosphinous acids are oxidised by nitric acid.

(3) By treating the compounds $RPCl_4$ and $RPOCl_2$ with water.

The last two methods are the most general ones, but several specialised methods have been devised for specific cases.

The acids are solids, the lower members being deliquescent. They readily form salts, and treatment with phosphorus pentachloride yields the oxychlorides, $RPOCl_2$, which are also formed when the tetrachlorides $RPCl_4$ are allowed to react with sulphur dioxide.

Methylphosphinic acid, $CH_3.PO(OH)_2$, may be prepared in several ways: (1) A slow stream of pure methylphosphine is passed into fuming nitric acid;[2] the gas must contain no free phosphine or explosion occurs. The liquid is evaporated several times on the water-bath to remove nitric acid and the residue is then boiled with lead oxide to remove phosphoric acid. The lead salts are treated with acetic acid, when the phosphinate dissolves, leaving the phosphate as a residue. The acetic acid solution is treated with hydrogen sulphide, which removes the lead as sulphide, and the filtrate on evaporation on the water-bath gives an oil which solidifies on cooling. (2) Diphenyl phosphite and 1 molecular equivalent of methyl iodide are heated together on the water-bath for forty-eight hours. The resulting product is shaken with dilute sodium hydroxide solution, when diphenyl methylphosphinate results. This ester is then saponified by means of alcoholic potassium hydroxide or fuming nitric acid.[3] (3) By heating triethyl phosphite with methyl iodide at 220° C., the chief by-products being ethyl iodide and ethylene, and small quantities of phosphorous and phosphoric acids.

The crystals of the acid are hygroscopic, M.pt. 105° C., readily soluble in water or alcohol, less soluble in ether, unaffected by fuming nitric acid. The *silver salt*, $CH_3.PO(OAg)_2$, is a white, amorphous precipitate, insoluble in water; the *lead salt*, $CH_3.PO_3Pb$, is a white amorphous powder, insoluble in water or acetic acid; the *barium salt*, $CH_3.PO_3Ba$, forms microscopic needles from dilute alcohol, readily soluble in water. The *diethyl ester* of the acid, $CH_3.PO(OC_2H_5)_2$, is

[1] Guichard, *Ber.*, 1899, **32**, 1572.
[2] Hofmann, *Ber.*, 1872, **5**, 104.
[3] Michaelis and Kähne, *Ber.*, 1898, **31**, 1050.

obtained by the interaction of methyl iodide and triethyl phosphite at room temperature;[1] it is a liquid of pleasant odour, B.pt. 192° to 194° C. at 763 mm., density 1·0726 at 0° C., 1·0508 at 23° C., and is readily soluble in water. Methylphosphinic acid reacts with two molecular equivalents of phosphorus pentachloride to yield an *acid chloride*, $CH_3.POCl_2$, a crystalline compound, M.pt. 32° C., B.pt. 163° C;[2] it is decomposed by water into methylphosphinic and hydrochloric acids, and with alcohol it yields methylphosphinic acid and ethyl chloride. The *diethylamide* of methylphosphinic acid, $CH_3.PO[N(C_2H_5)_2]_2$, is formed by decomposing diethylamine-N-ethoxyphosphine methiodide, $[(C_2H_5)_2N]_2P(CH_3I)OC_2H_5$. It is a colourless, aromatic oil,[3] B.pt. 145° to 148° C. at 22 mm., dissolving easily in alcohol or ether, sparingly soluble in water. The *dipropylamide*, $CH_3.PO[N(CH_2.CH_2.CH_3)_2]_2$, is the decomposition product of dipropylamine-N-ethoxyphosphine methiodide; it boils at 176° to 180° C. at 25 mm. and is soluble in ether.

Ethylphosphinic acid, $C_2H_5.PO(OH)_2$, is prepared as follows: (1) By the oxidation of ethylphosphine with nitric acid.[4] (2) By treating ethyldichlorophosphine with water and evaporating the resulting mixture with fuming nitric acid.[5] (3) The oxidation of ethylphosphinous acid by nitric acid yields the phosphinic acid.[6] (4) The compounds $C_2H_5.PCl_4$ and $C_2H_5.POCl_2$ are converted into ethylphosphinic acid when treated with water.

Ethylphosphinic acid yields hygroscopic crystals, M.pt. 44° C., very soluble in water; it can be distilled without decomposition.[7] Its *silver salt*, $C_2H_5.PO(OAg)_2$, is a yellow, amorphous powder, insoluble in water or alcohol. The *diethyl ester* is formed by warming sodium diethyl phosphite with ethyl iodide,[8] or by treating the oxychloride, $C_2H_5.POCl_2$, with sodium ethylate. The ester is a transparent liquid, B.pt. 90° to 95° C. at 20 mm. or 198° C. at 760 mm., density 1·025 at 21° C.; it has an odour resembling that of apples, and its aqueous solution does not reduce mercuric chloride. The *oxychloride*, $C_2H_5.POCl_2$, is obtained by the action of water on the tetrachloride, $C_2H_5.PCl_4$,[9] or by treating the tetrachloride with sulphur dioxide.[10] It boils normally at 175° C. or at 75° to 78° C. at 50 mm., and has a density of 1·1883 at 20° C. Water converts it into ethylphosphinic acid, and sodium ethylate yields the diethyl ester of ethylphosphinic acid.

n-Propylphosphinic acid, $CH_3.CH_2.CH_2.PO(OH)_2$, occurs when the corresponding phosphinous acid is oxidised by nitric acid or the tetrachloride decomposed by water.[11] It is isolated in the form of hygroscopic scales, soluble in water and melting at 66° C. The *diethyl ester* is the product of the interaction of propyl bromide and triethyl phosphite at about 160° C.;[12] it is a liquid, B.pt. 86° to 88° C. at 8·5 mm.,

[1] Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 687; *Chem. Zentr.*, 1906, ii, 1640.
[2] Hofmann, *Ber.*, 1873, 6, 306.
[3] Michaelis and Möttek, *Annalen*, 1903, 326, 164.
[4] Hofmann, *Ber.*, 1872, 5, 110.
[5] Michaelis, *Ber.*, 1880, 13, 2175.
[6] Guichard, *Ber.*, 1899, 32, 1572.
[7] Hofmann, *loc. cit.*
[8] Michaelis and Becker, *Ber.*, 1897, 30, 1003.
[9] Michaelis, *loc. cit.*
[10] Guichard, *loc. cit.*; Michaelis and Becker, *loc. cit.*
[11] Guichard, *loc. cit.*
[12] Arbusoff, *loc. cit.*

density 1·0467 at 0° C. or 1·0291 at 19° C. The *oxychloride*, $C_3H_7.POCl_2$, results when the tetrachloride, $C_3H_7.PCl_4$, is treated with sulphur dioxide; it boils at 88° to 90° C. at 50 mm., and has a density of 1·3088 at 20° C.

iso-Propylphosphinic acid, $(CH_3)_2CH.PO(OH)_2$.—This acid may be obtained by the two methods just described for the normal acid or by the oxidation of *iso*propylphosphine in hydrochloric acid solution with nitric acid.[1] It is a white, paraffin-like mass, M.pt. 71° C.,[2] forming a *silver salt*, $C_3H_7.PO(OAg)_2$, a white, amorphous precipitate. The *oxychloride*, $C_3H_7.POCl_2$, boils at 82° to 84° C. at 50 mm., and has a density of 1·3018 at 20° C.

iso-Butylphosphinic acid, $(CH_3)_2.CH.CH_2.PO(OH)_2$, is prepared by similar methods to the preceding compounds. It crystallises in scales, M.pt. 124° C., and yields a *silver salt* as a white precipitate. The corresponding *oxychloride*, $C_4H_9.POCl_2$, is a liquid, B.pt. 104° to 108° C. at 50 mm., density 1·2333 at 20° C. The *phenyl hydrazide* of the *thio-acid*, $C_4H_9.PS(N_2H_2C_6H_5)_2$, forms white leaflets, M.pt. 128° C.

iso-Amylphosphinic acid, $C_5H_{11}.PO(OH)_2$, can be prepared by the general methods, and also occurs when *iso*amylphosphinous acid is heated at 60° to 135° C., *iso*amylphosphine being formed as a by-product. It crystallises in plates, M.pt. 160° C.,[3] 166° C.,[4] sparingly soluble in cold water, readily soluble in hot water or alcohol. It gives an amorphous *silver salt* of normal constitution. An *anhydride* of the acid, $C_5H_{11}PO_2$, may be prepared by boiling the oxychloride, $C_5H_{11}.POCl_2$, with the acid in dry light petroleum; the resulting product consists of small, hard crystals, M.pt. 122° C., readily soluble in benzene. The *oxychloride* is a liquid, B.pt. 122° to 125° C. at 55 mm., density 1·1883 at 20° C. The *phenyl ester* of *iso*amylphosphinic acid is a heavy liquid, undecomposed by water, and the *phenyl hydrazide*, $C_5H_{11}.PO(N_2H_2C_6H_5)_2$, is a light, white powder, M.pt. 134° to 135° C., readily soluble in alcohol or ether. *Isoamylthiophosphinic acid* has not been isolated in the pure state, but its *diethyl ester* is known, $C_5H_{11}.PS(OC_2H_5)_2$. This is formed by the action of alcoholic sodium ethylate on the *thio-chloride* $C_5H_{11}.PSCl_2$.[5] It is a pale yellow liquid of peculiar odour, B.pt. 250° to 255° C., density 0·9848 at 20° C.

n-Heptylphosphinic acid, $CH_3.(CH_2)_5.CH_2.PO(OH)_2$.—This acid is formed by heating α-hydroxy-*n*-heptylphosphinic acid with 10 parts of fuming hydriodic acid at 200° C.[6] It melts at 106° C., and with a little water swells up into a gelatinous mass. It is soluble in alcohol, ether and petroleum ether.

Hydroxyalkylphosphinic Acids.

The following is a general method of preparation for hydroxyphosphinic acids:[7] Phosphorus trichloride (at least a 10 per cent. excess) is added to the carbonyl compound (aldehyde or ketone) below 35° C.; sometimes cooling is necessary. The mixture is protected from moisture

[1] Hofmann, *Ber.*, 1873, 6, 303.
[2] Guichard, *loc. cit.*
[3] Hofmann, *loc. cit.*; compare Auger, *Compt. rend.*, 1904, 139, 639; Fossek, *Monatsh.*, 1886, 7, 20.
[4] Guichard, *loc. cit.*
[5] Guichard, *loc. cit.*
[6] Fossek, *loc. cit.*
[7] Conant, MacDonald and Kinney, *J. Amer. Chem. Soc.*, 1921, 43, 1928.

and allowed to stand for two to three hours. A slight excess of glacial acetic acid is then added, the temperature being maintained at 20° to 30° C. After twelve hours the mixture is poured into 300 c.c. of ice-water and the whole vigorously shaken. The solution is then evaporated and the gum allowed to crystallise, which may take from one to fourteen days. The mass is then dried on a plate and finally in a vacuum desiccator over sodium hydroxide. In cases where no crystallisation takes place, the lead salt is prepared as follows: The gum is dissolved in about 200 c.c. of water, making strongly alkaline with ammonium hydroxide, and magnesium nitrate added. After standing overnight the precipitated magnesium ammonium phosphate is removed, the solution diluted to 500 c.c., made faintly acid with acetic acid and heating to boiling. A solution of lead acetate or nitrate is then added in excess and the whole boiled for five to ten minutes, then filtered. The lead salt is washed with boiling water and dried, the product thus obtained being free from phosphate and practically free from chloride.

Hydroxymethylphosphinic acid, $HO.CH_2.PO(OH)_2$.—This acid is said to result from the interaction of trioxymethylene and phosphorus trichloride.[1] It crystallises in white, rectangular plates, very hygroscopic and deliquescent, and it is a dibasic acid. The following salts are known: *barium salt*, pearly plates; *silver salt*, white amorphous powder; *pyridinium salt*, $HO.CH_2.PO(OH)_2.C_5H_5N$, glistening needles, M.pt. 105° C.; *calcium*, *lead* and *zinc salts*, white, amorphous powders; *copper salt*, pale blue; *ferric salt*, pale yellow; *calcium* and *barium hydrogen salts* cannot be obtained in solid form.

α-Hydroxyisopropylphosphinic acid, $(CH_3)_2C(OH).PO(OH)_2$, may be isolated as follows: (1) By the general method already given, the yield being about 91 per cent.[2] (2) It occurs in small quantities in the interaction of acetone and crystallised hypophosphorous acid, the main product of the reaction being hydroxy*iso*propylhypophosphorous acid. (3) Hydroxy*iso*propylhypophosphorous acid may be oxidised to the phosphinic acid in the following manner:[3] The lead salt is dissolved in water and the lead removed by passing in hydrogen sulphide and filtering off the lead sulphide. Dissolved hydrogen sulphide is driven off by heating the solution, and two molecular equivalents of mercuric chloride added. The excess of the latter is removed by hydrogen sulphide, the filtrate evaporated to dryness and the residue recrystallised from acetic acid. White, air-stable crystals result, melting with decomposition at 175° C.[4]

The acid dissolves in water and aqueous acetone, is less soluble in alcohol and ethyl acetate, sparingly soluble in anhydrous acetone, and insoluble in ether, chloroform, carbon disulphide and ligroin. It is monobasic towards methyl orange, dibasic towards phenolphthalein. The aqueous solution on prolonged boiling with dilute acid is decomposed, but it is stable towards alkali. A number of salts is known: *sodium salt*, $NaC_3H_8O_4P.6H_2O$, decomposed above 210° C. with evolution of phosphine;[5] *sodium salt*, $NaC_3H_8O_4P.4H_2O$, efflorescent, and

[1] Page, *Trans. Chem. Soc.*, 1912, 101, 423.

[2] Conant, MacDonald and Kinney, *loc. cit.*

[3] Marie, *Compt. rend.*, 1901, 133, 121; *ibid.*, 1902, 134, 847; *Ann. Chim. Phys.*, 1904, [8], 3, 347, 371.

[4] Conant, MacDonald and Kinney give the melting-point as 167° to 169° C.; compare Fossek, *Monatsh.*, 1886, 7, 20.

[5] Marie, *Compt. rend.*, 1902, 134, 994; *Ann. Chim. Phys.*, 1904, [8], 3, 376, 380.

unlike the preceding salt not precipitated from its aqueous solution by alcohol; it loses its water of crystallisation at 100° C. and evolves phosphine above 220° C.; *copper salt*, $Cu(C_3H_8O_4P)_2.2C_2H_5OH$, pale blue plates, efflorescing in air and losing its alcohol at 100° C., the colour changing to white; *copper salt*, $CuC_3H_7O_4P.H_2O$, greenish-blue needles, becoming green and anhydrous at 150° C., insoluble in water; *silver salt*, $Ag_2C_3H_7O_4P$, a white, crystalline precipitate, readily soluble in nitric acid; *lead salt*, plates, soluble in about 3000 parts of hot or 1000 parts of cold water, very soluble in dilute nitric acid. The *dimethyl ester* is prepared by treating the silver salt of the acid with methyl iodide.[1] It forms colourless crystals, M.pt. 76° C., losing acetone when distilled *in vacuo*. The *diethyl ester* melts at 14° to 15° C., and boils at 145° C. at 20 mm. with slight decomposition; it behaves in a similar manner to the dimethyl ester when heated *in vacuo*. The *diphenyl ester* may be obtained in the following manner: 10 grams of diphenoxychlorophosphine are treated with 2·5 grams of acetone. Heat is evolved during the process and 6 c.c. of glacial acetic acid are added and the whole allowed to stand for twelve hours. The mixture is then poured into water, the ester dissolved in ether, and the ether evaporated off. The resulting pasty mass, after drying on a porous plate, is recrystallised from petroleum ether, 4·5 grams of the compound, M.pt. 113° to 114° C., being isolated.[2] The *acetyl derivative* of the *diphenyl ester* melts at 72° to 72·5° C.

α-Hydroxy-α-methylpropylphosphinic acid or **β-Hydroxyisobutylphosphinic acid**, $(CH_3)(C_2H_5)C(OH).PO(OH)_2$, is best obtained by the general method of preparation. It also occurs along with hydroxybutylhypophosphorous acid when methyl ethyl ketone reacts with hypophosphorous acid or when hydroxybutylhypophosphorous acid is oxidised by bromine.[3] It crystallises from methyl alcohol or acetone in plates, M.pt. 158° to 159° C.,[4] readily soluble in water, alcohol or hot acetic acid, sparingly soluble in chloroform or acetone, insoluble in ether. It yields a *benzoyl derivative*. The *lead salt*, $C_2H_5.C(PO_3Pb)OH.CH_3$, is insoluble in water, moderately soluble in concentrated nitric acid. The *diphenyl ester* is obtained by the interaction of 3 grams of methyl ethyl ketone, 10 grams of diphenoxychlorophosphine and 3 c.c. of glacial acetic acid. The reaction is complete in about two days at room temperature,[5] about 5 grams of ester being obtained, M.pt. 128·5° C.

α-Hydroxy-α-methylbutylphosphinic acid, $(CH_3)(C_3H_7)C(OH).PO(OH)_2$, is formed by the oxidation of the corresponding hypophosphorous acid with bromine.[6] It separates from acetone as a colourless, crystalline mass, M.pt. 139° to 140° C., soluble in the usual organic solvents with the exception of ether.

α-Hydroxy-α-ethylbutylphosphinic acid, $(C_2H_5)(C_3H_7)C(OH).PO(OH)_2$, is isolated in the form of its *lead salt* when ethyl propyl ketone is used in the general process for preparing hydroxyphosphinic acids.[7]

[1] Marie, *Compt. rend.*, 1902, 135, 106; *Ann. Chim. Phys.*, 1904, [8], 3, 383.
[2] Conant, Wallingford and Gandheker, *J. Amer. Chem. Soc.*, 1923, 45, 762.
[3] Marie, *Compt. rend.*, 1903, 136, 234; *Ann. Chim. Phys.*, 1904, [8], 3, 391.
[4] Compare Fossek, *Monatsh.*, 1884, 5, 627.
[5] Conant, Wallingford and Gandheker, *loc. cit.*
[6] Marie, *Compt. rend.*, 1903, 136, 509; *Ann. Chim. Phys.*, 1904, [8], 3, 395.
[7] Conant, MacDonald and Kinney, *loc. cit.*

α-Hydroxyisoamylphosphinic acid, $(CH_3)_2CH.CH_2.CH(OH).PO(OH)_2$, may be prepared in three ways : (1) Phosphorus trichloride (1 gram-molecule) is carefully added to four molecular equivalents of *iso*valeraldehyde and the unstable oil which results is decomposed with twenty times its weight of water. Two layers are obtained, the upper one containing two-thirds of the aldehyde employed, the lower one containing a solution of the hydroxyphosphinic acid.[1] (2) By heating *iso*valeraldehyde with hypophosphorous acid and oxidising the reaction product with bromine.[2] (3) By heating *iso*valeraldehyde with phosphorous acid.

The acid crystallises in hexagonal plates when its alcohol solution is slowly evaporated ; the crystals sinter at 183° to 184° C. and melt at 191° C. Dry distillation of the product yields *iso*valeraldehyde, phosphine and phosphoric acid. The acid is incompletely decomposed by nitric acid or aqua regia, and is not attacked when boiled with aqueous alkalis. Potassium permanganate converts it into *iso*valeraldehyde and phosphoric acid, and hydriodic acid reduces it to *iso*amylphosphinic acid. Phosphorus pentachloride reacts to form a *trichloride*, $(CH_3)_2CH.CH_2.CHCl.POCl_2$, a syrupy liquid, B.pt. 106° to 109° C. at 12 mm. Water converts this chloride into *chloroisoamylphosphinic acid*, $(CH_3)_2CH.CH_2.CHCl.PO(OH)_2$, a white precipitate, insoluble in water. This chloro-acid on solution in alcohol and subsequent evaporation yields a *diethyl ester* as a yellowish oil. The following salts of α-hydroxy-*iso*amylphosphinic acid are known : *acid barium salt*, $(C_5H_{12}O_4P)_2Ba$, stellate groups from water ; *normal barium salt*, $C_5H_{11}O_4PBa.2H_2O$, white crystalline powder, more soluble in cold than in hot water ; the *calcium salts* are similar to those of barium ; *silver salt*, $C_5H_{11}O_4PAg_2$, white caseous precipitate ; *lead salt*, $C_5H_{11}O_4PPb$, resembling silver salt.

α - Hydroxy - n - heptylphosphinic acid, $CH_3[CH_2]_5CH(OH).PO(OH)_2$, is the result of the interaction of phosphorus trichloride and œnanthol.[3] It separates from water in monoclinic crystals,[4] sintering at 165° C. and melting at 185° C.[5] It is insoluble in hot water and sparingly soluble in cold water. The *calcium salt*, $C_7H_{15}O_4PCa$, is a white precipitate. Reduction by hydriodic acid converts the hydroxy-acid to *n*-heptylphosphinic acid.

α - Hydroxy - α - methyl - β - dimethylpropylphosphinic acid, $(CH_3)_3C.C[PO(OH)_2]OH.CH_3$, is only known in the form of its lead salt. The latter is very hygroscopic and is produced by the general method, pinacolin being the carbonyl compound employed.[6]

α-Hydroxy-α-methyl-β-chloroethylphosphinic acid occurs in the form of its *diphenyl ester*, $CH_2Cl.C(CH_3)(OH)PO(OC_6H_5)_2$, when 5 grams of chloroacetone, 14 grams of diphenoxychlorophosphine and 6·5 grams of benzoic acid are mixed and allowed to stand for two days. The ester separates in the form of white, cubic crystals (1 gram), melting at 119° C.

[1] Fossek, *Monatsh.*, 1884, 5, 121, 627. Compare Page, *Trans. Chem. Soc.*, 1912, 101, 423.
[2] Marie, *Compt. rend.*, 1903, 136, 48; *Ann. Chim. Phys.*, 1904, [8], 3, 408.
[3] Fossek, *Monatsh.*, 1886, 7, 20.
[4] Zepharovich, *ibid.*, 1886, 7, 28.
[5] Conant, MacDonald and Kinney (*loc. cit.*) give the melting-point as 165° to 173° C.
[6] Conant, MacDonald and Kinney, *loc. cit.*

Compounds of the Type $R_2PO.OH$.

Our present knowledge of this class of acids is confined to the methyl and ethyl compounds, both of which may be isolated by dissolving the corresponding secondary phosphine in hydrochloric acid, adding fuming nitric acid and boiling the mixture. The silver salts are definite crystalline compounds, but free diethylphosphinic acid has not been obtained in the solid state.

Dimethylphosphinic acid, $(CH_3)_2PO.OH$.—A solution of dimethylphosphine in hydrochloric acid is mixed with fuming nitric acid and heated to boiling.[1] The solution is then evaporated several times with hydrochloric acid to remove the nitric acid, the hydrochloric acid removed by adding silver nitrate, and the filtrate from the silver chloride treated with hydrogen sulphide, then evaporated on the water-bath. Colourless crystals separate, but these become pale brown in contact with the air. They are very soluble in water, alcohol or ether, melt at about 76° C., and at high temperatures are volatile without decomposition. The *silver salt*, $(CH_3)_2PO(OAg)$, crystallises as fine white needles, having an extraordinary solubility in water, but only slightly soluble in alcohol or ether. A *barium* and a *lead salt* have been described, but not analysed. The acid is converted by one equivalent of phosphorus pentachloride into the *acid chloride*, $(CH_3)_2POCl$, which is a crystalline product, M.pt. 66° C., B.pt. 204° C., reconverted to the acid by water or alcohol.[2]

Diethylphosphinic acid, $(C_2H_5)_2PO.OH$.—This acid is prepared in a similar manner to the preceding dimethyl acid. It cannot be obtained in the solid state, being liquid even at −25° C. Its *silver salt*, $(C_2H_5)_2PO(OAg)$, crystallises in fine, matted needles.

Diethyldithiophosphinic acid,[3] $(C_2H_5)_2PS.SH$.—When 1 gram-molecule of diethylphosphine is mixed with 2 equivalents of sulphur in ether solution, the sulphur gradually dissolves and crystals separate (see below). The mother liquor from these crystals is boiled with a slight excess of ammonium hydroxide, when more crystals are formed and removed whilst the liquid is hot. The solution as it cools deposits triethylphosphine sulphide, which is removed and the cold solution then concentrated. Crystals of *ammonium diethyldithiophosphinate* separate, melting at 193° C., decomposing a little above this temperature, but subliming on rapid heating. The salt is readily soluble in water and alcohol, the aqueous solution giving amorphous precipitates with silver, copper and lead salts. With hydrochloric acid the ammonium salt is converted into the *free acid*, an oil readily dissolving in alcohol or ether, insoluble in and heavier than water. The acid is not volatile in steam and is a strong acid. The *silver salt*, $(C_2H_5)_2PS.SAg$, forms white needles, insoluble in cold alcohol and stable at 100° C. The *benzyl derivative*, $(C_2H_5)_2PS.SC_7H_7$, melts at 54° C., is insoluble in water, but dissolves in the usual organic solvents.

Diethyldithiophosphinic acid persulphide, $(C_2H_5)_2PS.S.S.S.PS(C_2H_5)_2$.—This compound is formed as a by-product in the preparation of the preceding acid. It separates out in crystalline form, as mentioned already, at the commencement of the reaction. The formula

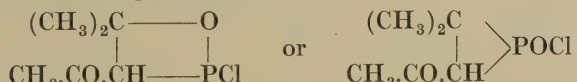
[1] Hofmann, *Ber.*, 1872, **5**, 104.
[2] Hofmann, *ibid.*, 1873, **6**, 307.
[3] Hofmann and Mahla, *Ber.*, 1892, **25**, 2436.

assigned to the crystals is that of a persulphide, as shown. It separates from carbon disulphide in hard, white, hexagonal prisms, M.pt. 105° C. Freshly prepared ammonium sulphide converts it on warming into ammonium diethyldithiophosphinate, with liberation of free sulphur.

By oxidation of the corresponding phosphines the following acids are said to be derived, all of which are described as water-insoluble oils:[1] *dipropylphosphinic acid*, *di-isobutylphosphinic acid*, and *di-isoamylphosphinic acid.*

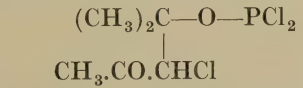
Phosphorus Compounds Derived from Aldehydes and Ketones.

Diacetone chlorophosphine,[2]



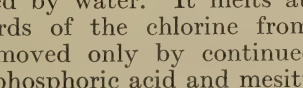
To a mixture of 500 grams of phosphorus trichloride and 2 to 2·5 volumes of acetone (free from methyl alcohol), 80 grams of anhydrous aluminium chloride are added. A brisk reaction occurs, hydrogen chloride is evolved and the mixture requires cooling. After the gas evolution has ceased, ligroin is added and the product filtered. The filtrate is heated on the water-bath, and after a time the solvent is removed and the residue fractionated *in vacuo*. The main product distils at 154° C. at 100 mm., and on cooling crystallises. The crystals are colourless, strongly refractive, and melt at 35° to 36° C., B.pt. 154° C. at 100 mm. or 235° C. at 745 mm., density 1·209 at 17·5° C. Water converts the compound into diacetone phosphinic acid, and alcohol yields the corresponding ester. The chlorophosphine is soluble without decomposition in ether and light petroleum, and is not completely decomposed by nitric acid. It combines directly with chlorine and bromine (2 atoms), and bromine water converts the whole of the phosphorus to phosphoric acid.

Diacetone phosphorus trichloride,



This product is formed when a ligroin solution of the foregoing chlorophosphine is treated with dry chlorine. It is soluble in light petroleum and ether, but less soluble than the chlorobromide (see below), and is more slowly attacked by water. It melts at 115° C. Silver nitrate precipitates two-thirds of the chlorine from aqueous solution, the remainder being removed only by continued boiling; the solution remaining contains phosphoric acid and mesityl oxide.

Diacetone phosphorus chlorobromide,



The foregoing chlorophosphine in ligroin solution is treated dropwise with a solution of bromine in the same solvent. The precipitated

[1] Hofmann, *loc. cit.*

[2] Michaelis, *Ber.*, 1884, 17, 1273; 1885, 18, 898.

product is washed with ligroin, then with a little ether. It is a colourless, crystalline mass, fuming slightly in contact with air, melting at 142° C., sparingly soluble in ligroin, readily soluble in ether. It is slowly decomposed by water into hydrochloric and hydrobromic acids, mesityl oxide and phosphoric acid.

Diacetone phosphinic acid or **2-Methylpentanone-(4)-phosphinic acid-(3)**,[1] $(CH_3)_2CH.CH(CO.CH_3).PO(OH)_2$.—This acid is formed when diacetone chlorophosphine is decomposed by water. It crystallises from water in fine needles containing 1 molecule of solvent, M.pt. 63° to 64° C., 100° to 110° C. when anhydrous. It is very easily soluble in water or alcohol, soluble with difficulty in ether. The phosphorus is removed by heating with bromine water, and the oxidation product with fuming nitric acid is described below. The *potassium salt*, $C_6H_{11}OPO_3HK$, is a resinous mass, dissolving in water and alcohol. It results when an alcohol solution of potassium hydroxide is added to an alcohol solution of the acid; if an excess of the acid be used, an *acid potassium salt* is formed, $C_6H_{11}OPO_3HK.C_6H_{11}OPO_3H_2$, consisting of needles, readily soluble in water, sparingly soluble in alcohol. The *ammonium salt*, $C_6H_{11}OPO_3H(NH_4)$, is soluble in water, but practically insoluble in alcohol; if alcoholic ammonia is used in the preparation of the salt, a white, crystalline precipitate is produced, which corresponds to the formula, $C_6H_{11}OPO_3(NH_4)_2.C_6H_{11}OPO_3H(NH_4).2H_2O$. The *silver salt*, $C_6H_{11}OPO_3Ag_2$, is a white precipitate, and the *magnesium salt*, $C_6H_{11}OPO_3Mg.6H_2O$, crystallises in plates, sparingly soluble in hot and cold water. The *normal barium salt*, $C_6H_{11}OPO_3Ba.6H_2O$, crystallises in colourless leaflets, described as rhombic-bipyramidal;[2] it is sparingly soluble in cold water, somewhat soluble in hot water. This latter salt is formed from barium hydroxide, but if barium carbonate replaces the latter, the salt obtained has the constitution $(C_6H_{12}O_4P)_2Ba.2H_2O$; this form separates in fine needles, very easily soluble in water, sparingly soluble in alcohol. A *hydrate* of constitution $C_6H_{11}OPO_3Ba.4{\cdot}5H_2O$ is also known. The *lead salt*, $2C_6H_{11}OPO_3Pb.PbO$, is a white powder.

The presence of the carbonyl group in the phosphinic acid is shown by the fact that the acid forms an oxime; moreover, only one oxime is produced, and therefore only one carbonyl grouping exists in the molecule. The *oxime*, $(CH_3)_2CH.CH[C(CH_3) : NOH]PO(OH)_2$, is produced by boiling an aqueous solution of the acid with 1 molecular equivalent of hydroxylamine hydrochloride and 0·5 of an equivalent of sodium carbonate for six hours; it separates from water in colourless crystals, M.pt. 169° to 170° C. with decomposition; it is a strong dibasic acid, fairly soluble in water and alcohol, less soluble in ether.

isoPropylphosphino-carboxylic acid or **Propane-β-carboxylic acid α-phosphinic acid**, $HOOC.CH(CH_3).CH_2PO(OH)_2$.[3]—This acid results when diacetone phosphinic acid is warmed with fuming nitric acid. The mixture is treated with barium hydroxide and the barium salt extracted from the precipitate by cold water. The *barium salt*, $(C_4H_6O_5P)_2Ba_3$, is more soluble in cold than hot water, and crystallises in shining plates. The *free acid* forms a colourless mass, readily soluble in water, alcohol or ether. The *silver salt*, $C_4H_6O_5PAg_3$, is a white, crystalline precipitate, soluble in nitric acid or ammonium hydroxide.

[1] Michaelis, *loc. cit.*
[2] Arzruni, *Ber.*, 1885, **18**, 904; see Groth, *Ch. Kr.*, **3**, 452.
[3] Michaelis, *loc. cit.*

Condensation Products of Hypophosphorous Acid.

α-Hydroxyisopropylhypophosphorous acid, $(CH_3)_2C(OH).PHO.OH$.—A solution of 250 grams of crystallised hypophosphorous acid in 400 c.c. of acetone is boiled for several days. The filtrate on cooling deposits *bis*-α-hydroxy*iso*propylhypophosphorous acid, which is removed. The acetone is removed from the mother liquor, the residue diluted with water, neutralised with lead carbonate and the insoluble lead salt of the α-hydroxy*iso*propylphosphinic acid filtered off. The filtrate is evaporated to dryness, the residue taken up in 95 per cent. alcohol containing a few c.c. of water, when on cooling crystalline crusts separate. These are dissolved in water and treated with hydrogen sulphide, the filtrate from this reaction being evaporated in the absence of air.[1] The acid is purified by treating it in the molten state with dry ether, until no further rise in the melting-point is noted.[2]

The acid is extremely hygroscopic and melts at 52° C. It is soluble in alcohols, acetone and ethyl acetate, but insoluble in benzene, ether and petroleum ether. It is monobasic and decomposes carbonates. Heating at 110° to 120° C. or prolonged boiling of its aqueous solution in the presence of concentrated acid decomposes it into acetone and hypophosphorous acid. It is readily oxidised to α-hydroxy*iso*propylphosphinic acid, and prolonged boiling with acetone gives *bis*-α-hydroxy*iso*propylphosphinous acid. Aldehydes condense to form hydroxyalkyl-α-hydroxy*iso*propylhypophosphorous acids.[3] The following salts of the acid have been obtained: *copper salt*, $(C_3H_8O_3P)_2Cu.H_2O$, a pale blue mass, stable at ordinary temperatures, decomposed when heated in a carbon dioxide atmosphere at 100° C. or when its concentrated aqueous solution is heated above 60° C.[4] The decomposition takes place according to the equation

$$[(CH_3)_2C(OH).PHO.O]_2Cu.H_2O = (CH_3)_2C(OH)PHO.OH + (CH_3)_2C(OH).PO(OH)_2 + Cu$$

The *silver salt*, $C_3H_8O_3PAg$, forms colourless crystals, decomposing with explosion at 90° C., and yielding a very unstable aqueous solution which decomposes in a similar manner to the copper salt. The *lead salt*, $(C_3H_8O_3P)_2Pb$, separates as a starry mass of crystals, very soluble in water or aqueous alcohol, insoluble in absolute alcohol. The *cobalt salt*, $(C_3H_8O_3P)_2Co.4H_2O$, forms rose-coloured, bushy crystals, becoming blue and anhydrous at 100° C., and the *nickel salt*, $(C_3H_8O_3P)_2Ni.4H_2O$, separates as a pale green precipitate, losing its water at 100° C., changing to yellow; it is not decomposed below 200° C. The *methyl ester* of the acid is obtained by treating the silver salt with methyl iodide. It is a fairly mobile liquid, completely decomposed when distilled *in vacuo*. Its density at 16·5° C. is 1·212 and the refractive index at 16° C. is 1·462. The physical constants for the *ethyl ester* are as follows: density 1·122 at 22·5° C., n_D 1·452 at 18·5° C. The condensation product with acetaldehyde, namely, *hydroxyethyl-hydroxyisopropylhypophosphorous acid*, $[(CH_3)_2C(OH)][CH_3.CH(OH)]PO.OH$, crystallises

[1] Marie, *Compt. rend.*, 1901, 133, 220; *Ann. Chim. Phys.*, 1904, [8], 3, 347, 363.
[2] Marie, *Compt. rend.*, 1902, 134, 286.
[3] Marie, *Compt. rend.*, 1904, 138, 1708; *Ann. Chim. Phys.*, 1904, [8], 3, 419.
[4] Marie, *Compt. rend.*, 1902, 134, 287; *Ann. Chim. Phys.*, 1904, [8], 3, 366.

from acetone and melts at 132° C. ; it is soluble in alcohols, insoluble in ether, chloroform or benzene.[1]

Bis-α-hydroxyisopropylhypophosphorous acid, $(CH_3)_2C(OH).PO(OH).C(OH)(CH_3)_2$, is prepared by boiling a solution of 250 grams of hypophosphorous acid in 400 grams of acetone for many days.[2] The product separates on cooling, and recrystallisation from boiling alcohol yields crystals, M.pt. 185° C., soluble in water, alcohol, acetone and chloroform, insoluble in ether or carbon disulphide. It is a strong monobasic acid, and readily decomposes carbonates. It readily yields acetone when heated at 150° C., or when boiled with acid or alkali.[3] When heated with mercuric chloride, the acid is slowly oxidised to α-hydroxy*iso*propylphosphinic acid. The following salts are known : *sodium salt*, $C_6H_{14}O_4PNa.3H_2O$, colourless, efflorescent crystals, soluble in alcohol, and losing water of crystallisation at 100° C. ; *silver salt*, $C_6H_{14}O_4PAg$, colourless needles, very susceptible to light, sparingly soluble in alcohol ; *lanthanum salt*, $(C_6H_{14}O_4P)_3La$, a crystalline substance, sparingly soluble in hot or cold water ; *lead salt*, $(C_6H_{14}O_4P)_2Pb.2H_2O$, efflorescent crystals, losing water at 100° C. At 22° C. 100 grams of water dissolve 27·6 grams of the lead salt, which is insoluble in alcohol. The *methyl ester*, obtained in the usual way from the silver salt and methyl iodide, melts at 92° C. ; it is readily soluble in the usual solvents, and distillation *in vacuo* causes decomposition, with formation of the methyl ester of hydroxy*iso*propylhypophosphorous acid, acetone, the methyl ester of phosphorous acid and phosphine. The *ethyl ester* melts at 95° C. The *diacetate* is prepared by warming the acid with acetic anhydride ; it separates from alcohol in crystals, M.pt. 171° C.

α-Hydroxyisobutylhypophosphorous acid, $(CH_3)(C_2H_5)C(OH).PHO.OH$, is prepared by the prolonged boiling of hypophosphorous acid with an excess of methyl ethyl ketone, the hydroxybutylphosphinic acid occurring as a by-product.[4] It is isolated by means of its lead salt, and is obtained as a colourless hygroscopic syrup, which does not solidify at −20° C. It dissolves in alcohol or acetone, and is oxidised by bromine to hydroxybutylphosphinic acid. The following salts are known : *copper salt*, $(C_4H_{10}O_3P)_2Cu.4H_2O$, blue crystals, soluble in water and alcohol, decomposing above 70° C. ; *silver salt*, $C_4H_{10}O_3PAg$, decomposing with explosion above 100° C. ; *lead salt*, $(C_4H_{10}O_3P)_2Pb$, a crystalline mass, sintering at 95° C., readily soluble in water.

α-Hydroxymethylbutylhypophosphorous acid, $(CH_3)(C_3H_7)C(OH).PHO.OH$, occurs when hypophosphorous acid is heated for some days with an excess of methyl propyl ketone.[5] It is a colourless syrup, yielding a crystalline *lead salt*, $(C_5H_{12}O_3P)_2Pb$, soluble in alcohol. Bromine readily oxidises the acid to the corresponding phosphinic acid.

α-Hydroxyisoamylhypophosphorous acid, $(CH_3)_2CH.CH_2.CH(OH).PHO.OH$.—20 grams of *iso*valeraldehyde are heated with 61·3 grams of hypophosphorous acid in 166 c.c. of water in a carbon dioxide stream at 85° to 90° C. for two days. The solution is then saturated with barium hydroxide, treated with carbon dioxide and

[1] Marie, *Compt. rend.*, 1904, 138, 1709; *Ann. Chim. Phys.*, 1904, [8], 3, 425.
[2] Marie, *Compt. rend.*, 1901, 133, 219; *Ann. Chim. Phys.*, 1904, [8], 3, 347, 349.
[3] Marie, *Compt. rend.*, 1901, 133, 818; *Ann. Chim. Phys.*, 1904, [8], 3, 350.
[4] Marie, *Compt. rend.*, 1903, 136, 234; *Ann. Chim. Phys.*, 1904, [8], 3, 389.
[5] Marie, *Ann. Chim. Phys.*, p. 509.

filtered. The filtrate is evaporated to dryness on the water-bath, and the residue, which contains the barium salt of the acid, is extracted with methyl alcohol and the free acid liberated by sulphuric acid.[1] It is a thick syrup, decomposing above 170° C., phosphine and *iso*valeraldehyde being amongst the resulting products. The acid reduces silver nitrate and gives a *barium salt*, $Ba(C_5H_{12}O_3P)_2.4H_2O$, crystallising in needles.

Bis-α-hydroxyisoamylhypophosphorous acid, $[(CH_3)_2CH.CH_2.CH(OH)]_2PO.OH$.—This acid occurs as a by-product in the preceding preparation, but may be better prepared by heating 20 grams of *iso*valeraldehyde with 7·7 grams of hypophosphorous acid in 21 c.c. of water. It crystallises in needles which commence to decompose at 160° C. and melt at 230° C. It dissolves easily in alcohol, is sparingly soluble in water, insoluble in ether, chloroform and benzene. It dissolves in dilute hydrochloric acid, but with dilute sulphuric acid at 135° C. it yields the aldehyde and hypophosphorous acid. Boiling with potassium hydroxide does not cause decomposition. The *potassium salt*, $C_{10}H_{22}O_4PK.3H_2O$, separates from alcohol in plates; the *barium salt*, $(C_{10}H_{22}O_4P)_2Ba.H_2O$, forms needles or crusts, very soluble in water, sparingly soluble in alcohol. Acetyl chloride reacts with the acid forming the *diacetate*, a syrup, very soluble in alcohol, ether, carbon disulphide and chloroform, insoluble in water.

α - Hydroxy - n - heptylhypophosphorous acid, $CH_3[CH_2]_5CH(OH).PHO.OH$.—A mixture containing 20 grams of œnanthol, 46·5 grams of hypophosphorous acid, 126 c.c. of water and 40 c.c. of 90 per cent. alcohol is heated at 85° to 90° C. in a stream of carbon dioxide for two days. The alcohol is then removed by warming the mixture and treating it with carbon dioxide. Water is added (15 to 20 parts), followed by lead acetate, and the precipitate decomposed by hydrogen sulphide. The aqueous solution is then extracted with ether, the ether solution yielding plates, M.pt. 55° to 57° C., very soluble in water, alcohol or ether, sparingly soluble in chloroform. The acid decomposes above 120° C., giving phosphine and œnanthol amongst other products. It reduces ammoniacal silver solutions, but is not affected by boiling with potassium hydroxide. The *barium salt*, $(C_7H_{16}O_3P)_2Ba$, gives microscopic needles, very sparingly soluble in water, insoluble in alcohol. The *acetyl derivative* is a viscous liquid.

Bis - α - hydroxy - n - heptylhypophosphorous acid, $CH_3[CH_2]_5CH(OH).PO(OH).CH(OH)[CH_2]_5CH_3$, occurs when 30 grams of œnanthol are heated with 9 grams of hypophosphorous acid in 25 c.c. of water and 30 c.c. of alcohol at 95° C. in a stream of carbon dioxide for two days. An equal volume of water is then added and the alcohol removed by carbon dioxide at 100° C. The product is precipitated by adding 10 to 15 parts of water, washed with water and purified by repeated solution in dilute potassium hydroxide and precipitation with hydrochloric acid.[2] The acid separates from alcohol in plates, insoluble in ether, chloroform and carbon disulphide, very sparingly soluble in water, easily soluble in boiling alcohol. It decomposes towards 160° C., phosphine and œnanthol being identified amongst the products, and decomposition by dilute sulphuric acid at 135° C. gives œnanthol and hypophosphorous acid. The *potassium salt*, $C_{14}H_{30}O_4PK.4H_2O$, separates from alcohol in plates, the *barium salt*,

[1] Ville, *Ann. Chim. Phys.*, 1891, [7], 23, 330. [2] Ville, *ibid.*, p. 312.

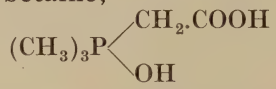
$(C_{14}H_{30}O_4P)_2Ba.3H_2O$, forms needles, and the *lead salt*, $(C_{14}H_{30}O_4P)_2Pb.3H_2O$, granular crystals, very sparingly soluble in water and alcohol. The *diacetate* separates from alcohol in microscopic needles, M.pt. 94° C., insoluble in water, readily soluble in alcohol, ether, carbon disulphide and chloroform.

α-Hydroxyisopropyl - α - hydroxy - n - heptylhypophosphorous acid, $(CH_3)_2C(OH).PO(OH).CH(OH)[CH_2]_5CH_3$, is obtained by the interaction of œnanthol and α-hydroxy*iso*propylhypophosphorous acid, p. 41.[1] It crystallises in plates, M.pt. 131° C., insoluble in cold water and ether, soluble in alcohol or acetone.

α-Hydroxy-sec.-butyl-α-hydroxy - n - heptylhypophosphorous acid, $(CH_3)(C_2H_5)C(OH).PO.OH.CH(OH)[CH_2]_5CH_3$, is the condensation product of œnanthol and α-hydroxy-*sec.*-butylhypophosphorous acid. It melts at 147° C., and has a similar solubility to the preceding compound.

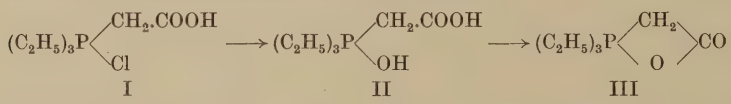
Alkyl Betaines containing Phosphorus.

Trimethylphosphobetaine,[2]



When equimolecular proportions of trimethylphosphine and monochloracetic acid are heated together in a sealed tube for five to six hours at 100° C., the main product of the reaction is a betaine, a small quantity of the hydrochloride of trimethylphosphine also resulting. The betaine is thus isolated in the form of its chloride, solution in water and addition of platinum chloride precipitating an orange-yellow *platinichloride*, $[(CH_3)_3P(Cl)(CH_2.COOH)]_2PtCl_4$. This salt is soluble in boiling water and separates in rhombic crystals on cooling. It is decomposed by hydrogen sulphide, giving the *chloride*, which is isolated as a deliquescent mass when the solution is concentrated. The chloride also forms an *aurichloride*, soluble in water and crystallising in long, yellow needles. The *base* is prepared by treating the chloride with sulphuric acid, removing the sulphate ion by means of barium hydroxide, and excess of the latter by passing carbon dioxide through the solution. The resulting product does not react with litmus, but yields salts with hydrochloric, nitric and hydriodic acids. The *iodide* separates from water in shining plates.

Triethylphosphobetaine hydrochloride,[3]



I II III

This chloride, I, is prepared by slowly adding triethylphosphine to monochloracetic acid and shaking the mixture. Owing to the rise of temperature it is necessary to cool the reaction mixture, a dense oily layer separating out. After about an hour the oil solidifies and is purified by solution in alcohol and precipitation with ether. The

[1] Marie, *Compt. rend.*, 1904, **138**, 1708; *Ann. Chim. Phys.*, 1904, [8], **3**, 420.
[2] Meyer, *Ber.*, 1871, **4**, 734.
[3] Hofmann, *Jahresber.*, 1862, p. 334; Letts, *Proc. Roy. Soc. Edin.*, 1881, **11**, 40; *Trans. Roy. Soc. Edin.*, 1881, **30**, 285.

chloride has a sour taste, an acid reaction, and is not perceptibly deliquescent. The *platinichloride* forms orange crystals which contain a molecule of water of crystallisation. The chloride is decomposed by heat into methyltriethylchlorophosphine and carbon dioxide :

$$(C_2H_5)_3P(Cl)(CH_2.COOH) = (C_2H_5)_3(CH_3)PCl + CO_2$$

Potassium hydroxide decomposes the chloride according to the equation

$$(C_2H_5)_3P(Cl)(CH_2.COOH) + 2KOH = (C_2H_5)_3PO + KCl + CH_3.COOK + H_2O$$

Silver oxide transforms an aqueous solution of the hydrochloride to *triethylphosphobetaine* (II). Concentration of the solution then yields very deliquescent crystals, which lose water after keeping for several months *in vacuo* over sulphuric acid, giving the *anhydride* (III). When an aqueous solution of the free base is concentrated by boiling, a solid mass remains which has a faint acid reaction and effervesces with acids ; it appears to be triethylmethylphosphonium acid carbonate, a compound isomeric with the base itself :

$$(C_2H_5)_3P(OH)CH_2.COOH = (C_2H_5)_3P(CH_3)O.COOH$$

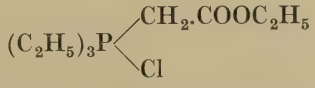
Potassium hydroxide decomposes the base in a similar manner to its action on the foregoing hydrochloride.

Triethylphosphobetaine hydrobromide, $(C_2H_5)_3P(Br)CH_2.COOH$, is best prepared by adding hydrobromic acid to a solution of the hydroxide. It forms thin quadratic plates, somewhat deliquescent, but otherwise resembling the hydrochloride. It should be noted that the hydrobromide is not prepared by treating triethylphosphine with bromacetic acid. In the latter case the products of reaction appear to be dependent upon the temperature. At low temperatures about equal proportions of triethylphosphobetaine hydrobromide and triethylphosphine acetobromide or a mixture of the latter with triethylphosphine bromacetate is obtained. At intermediate temperatures very little hydrobromide is formed and the product consists of acetobromide and bromacetate, whilst at higher temperatures the acetobromide is almost the sole product.

Triethylphosphobetaine hydriodide, $(C_2H_5)_3P(I)CH_2.COOH$, is prepared in a similar manner to the hydrobromide and yields small granular crystals.

Triethylphosphobetaine sulphate, $[(C_2H_5)_3P.CH_2.COOH]_2SO_4$, occurs when the hydrochloride is treated with silver sulphate and the resulting solution evaporated in a vacuum. A solid crystalline mass is obtained, which decomposes in a similar manner to the hydrochloride when heated.

Triethylphosphobetaine hydrochloride ethyl ester,



is isolated by the interaction of ethyl monochloracetate and triethylphosphine. A colourless syrup is formed, which rapidly solidifies, but cannot be recrystallised owing to its deliquescent nature. The *platinichloride* crystallises in light orange plates. Moist silver oxide reacts according to the following equations :—[1]

[1] Compare Hofmann, *Proc. Roy. Soc.*, 1860, 11, 550.

$$(C_2H_5)_3P(Cl)CH_2.COOC_2H_5 + AgOH = C_2H_5OH + AgCl + (C_2H_5)_3P\begin{matrix}CH_2\\ \diagup\quad\diagdown\\ O\quad\ \ CO\end{matrix}$$

$$(C_2H_5)_3P(Cl)CH_2.COOC_2H_5 + AgOH = AgCl + (C_2H_5)_3PO + CH_3COOC_2H_5$$

The hydrochloride is decomposed by potassium hydroxide as follows :

$$(C_2H_5)_3P(Cl)CH_2.COOC_2H_5 + KOH = KCl + (C_2H_5)_3PO + CH_3COOC_2H_5$$

Heat causes decomposition to take place with evolution of ethylene and carbon dioxide :

$$(C_2H_5)_3P(Cl)CH_2.COOC_2H_5 = (C_2H_5)_3(CH_3)PCl + CO_2 + C_2H_4$$

A *hydrobromide* and a *hydriodide* corresponding to the foregoing hydrochloride have also been isolated.

CHAPTER II.

AROMATIC PHOSPHINES AND PHOSPHONIUM COMPOUNDS.

Compounds of the Types RPH_2 and R_2PH.

The primary aryl phosphines are obtained by reducing the corresponding acids. They are all liquids with the exception of the mesityl-, diphenylmethane- and dibenzyl-compounds, which are low-melting solids. In air they rapidly undergo oxidation, yielding oxides and finally acids. When solutions of the phosphines in hydrochloric acid are treated with platinic chloride, crystalline platinichlorides result, $(RPH_2.HCl)_2PtCl_4$ or $(RPH_2)_2.H_2PtCl_6$. Solution in hydriodic acid converts the phosphines into their hydriodides, $RPH_2.HI$, yellow crystalline compounds. Only two derivatives of the type R_2PH are known, namely, diphenyl- and dibenzyl-phosphines. The former is the reduction product of diphenylchlorophosphine and the latter is a by-product in the preparation of benzylphosphine.

Phenylphosphine,

This substance is best prepared as follows : [1] Phosphorus-free phenyldichlorophosphine is shaken with an excess of alcohol and the solution filtered. The solvent is then distilled off in an atmosphere of carbon dioxide, the receiver changed and distillation in the inert gas continued, when phenylphosphine is obtained together with small amounts of benzene and diphenyl. The yield is about 60 per cent. The phosphine also results [2] from the following process : Dry hydrogen iodide is passed into phenyldichlorophosphine, the following reaction occurring :

$$C_6H_5.PCl_2 + 3HI = C_6H_5.PI_2.HI + 2HCl$$

The double compound distils above 360° C., but when cooled and treated dropwise with alcohol, a yellow liquid results, which yields phenylphosphine when fractionated in an atmosphere of hydrogen.

Phenylphosphine is a colourless, strongly refractive liquid, B.pt. 160° to 161° C., density 1·001 at 15° C. It possesses a vile odour. It readily oxidises in the air, yielding phenylphosphenoxide, but in contact with oxygen it inflames unless cooled. In water or concentrated acids it is only sparingly soluble, but explosion takes place on warming it with concentrated nitric acid. Dry hydrogen iodide yields phenylphosphonium iodide, and sulphur combines to form a sulphide, $C_6H_5.PH_2S$. Phenylphosphine in concentrated hydrochloric acid yields a *platinichloride* on addition of platinic chloride, $(C_6H_5.PH_2.HCl)_2PtCl_4$, a

[1] Kohler and Michaelis, *Ber.*, 1877, 10, 807.
[2] Michaelis, *Ber.*, 1874, 7, 6.

yellow crystalline substance, insoluble in water. The phosphine and *carbon disulphide* combine when heated together in a sealed tube at 150° C., forming the *product* $(C_6H_5.PHCS)_2S$ and hydrogen sulphide;[1] this sulpho-compound is readily soluble in carbon disulphide, sparingly soluble in alcohol and insoluble in water. Prolonged boiling with alcohol does not cause decomposition, but on heating the substance alone, hydrogen sulphide is evolved and a dark resin remains. The compound dissolves in alkalis, from which it is precipitated unchanged by acids. With chlorine it reacts according to the following equation :

$$(C_6H_5.PHCS)_2S + 6Cl_2 = C_6H_5.PCl_4 + C_6H_5.PSCl_2 + 2CSCl_2 + 2HCl$$

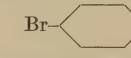
p-Chlorophenylphosphine,[2]

is obtained by dry distillation of the corresponding phosphinic acid, $ClC_6H_4.PO(OH)_2$, in a current of dry carbon dioxide. It forms a white crystalline mass, M.pt. 17° C., B.pt. 198° to 200° C., which oxidises in air and is converted by potassium hydroxide to the phosphinous acid salt :

$$ClC_6H_4.PH_2 + KOH + H_2O = ClC_6H_4.PO_2HK + 2H_2$$

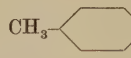
An emulsion of the phosphine in hydrochloric acid when treated with platinic chloride yields a *platinichloride*, $(ClC_6H_4.PH_2.HCl)_2PtCl_4$, a yellow crystalline powder, stable in air, and unmelted at 270° C.

p-Bromophenylphosphine,



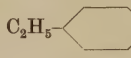
is a colourless, crystalline product, M.pt. 40° C., B.pt. 195° to 196° C. It possesses an intolerable odour, and rapidly oxidises in the air to the corresponding acid.[3]

p-Tolylphosphine,[4]



This phosphine is prepared in a similar manner to the phenyl compound and possesses similar properties to the latter. It melts at 4° C. and boils at 178° C. Its *hydriodide*, $C_7H_7.PH_2.HI$, is a yellow powder crystallising from fuming hydriodic acid in glistening needles which may be sublimed. The product is deliquescent and decomposed by water. The phosphine forms a yellow *platinichloride*, $(C_7H_7.PH_2.HCl)_2PtCl_4$.

p-Ethylphenylphosphine,[5]



is obtained by the reduction of the corresponding phosphinic acid by alcohol. It is a transparent, highly refractive liquid, B.pt. 200° C., possessing an intense objectionable odour and oxidised to the phosphinous acid on warming in air. The *platinichloride*, $(C_2H_5.C_6H_4.$

[1] Michaelis and Dittler, *Ber.*, 1879, **12**, 338.
[2] Michaelis, *Annalen*, 1896, **293**, 234.
[3] Michaelis, *loc. cit.*, p. 245.
[4] Michaelis and Paneck, *Annalen*, 1882, **212**, 233.
[5] Michaelis, *loc. cit.*

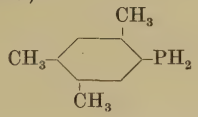
$PH_2.HCl)_2PtCl_4$, is a golden-yellow powder, insoluble in water, and the *methiodide*, $C_2H_5.C_6H_4.PH_2.CH_3I$, melts at 118° C.

Benzylphosphine,[1]

Benzyl chloride (2 molecular equivalents), phosphonium iodide (2 equivalents) and zinc oxide (1 equivalent) are heated together at 160° C., and the reaction mixture then distilled in steam, an oil heavier than water distilling over. After drying the crude product over potassium hydroxide, the oil is fractionated in hydrogen, the phosphine distilling at 180° to 190° C., further distillation giving a product of B.pt. 180° C. The residue left after the distillation contains dibenzylphosphine.

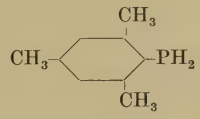
$$2C_6H_5.CH_2Cl + 2PH_4I + ZnO = 2C_6H_5.CH_2.PH_2.HI + ZnCl_2 + H_2O$$

Pseudocumylphosphine,[2]



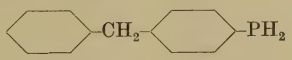
To obtain this, the corresponding dichlorophosphine is decomposed by water, the resulting acid treated with alcohol and the product distilled in a stream of carbon dioxide. It is a transparent liquid, B.pt. 214° to 218° C., rapidly oxidised in air. It is sparingly soluble in hydrochloric acid, the solution giving a yellow *platinichloride*, $(C_9H_{11}.PH_2)_2.H_2PtCl_6$, on treatment with platinic chloride.

Mesitylphosphine,



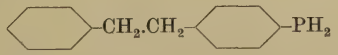
is obtained by the dry distillation of the corresponding phosphinous acid in a carbon dioxide atmosphere at 25 mm. pressure. It forms stout, colourless needles, M.pt. 40° C., B.pt. 125° C. at 25 mm., having a penetrating, unpleasant odour, and rapidly oxidising in air. Its *platinichloride*, $(C_9H_{11}.PH_2)_2.H_2PtCl_6$, separates from concentrated hydrochloric acid solution in shining orange crystals.

Diphenylmethanephosphine,



is a solid, M.pt. 46° C., B.pt. 184° C. at 20 mm., prepared in the usual manner. Its odour is less pungent than is the case with the foregoing compounds. It separates in the form of the *hydriodide* from hydriodic acid solution, this consisting of fine needles, M.pt. 134° C., decomposed by water.

Dibenzylphosphine,



melts at 75° C. and boils at 190° C. at 45 mm. It forms a crystalline methiodide.

[1] Hofmann, *Ber.*, 1872, 5, 100.

[2] Michaelis, *Annalen*, 1897, 294, 32.

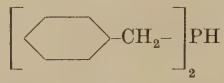
Diphenylphosphine,[1]

may be isolated in two ways : (1) By treating diphenylchlorophosphine with an excess of sodium carbonate in an atmosphere of hydrogen :

$$4(C_6H_5)_2PCl + 3Na_2CO_3 + H_2O = 2(C_6H_5)_2PH + 2(C_6H_5)_2PO_2Na + 3CO_2 + 4NaCl$$

(2) By heating diphenylchlorophosphine with zinc in a sealed tube at 230° C., then decomposing the resulting mixture with water. It is a colourless, viscous, pungent liquid, B.pt. 280° C., density 1·07 at 16° C., exposure to air or heating it with nitric acid causing it to oxidise. It acts as a weak base, its salts being decomposed by water. It combines with methyl iodide, acetyl chloride, hydrogen iodide and dry hydrogen chloride ; the compound formed in the latter case is not stable in air, but it yields a *platinichloride*, $[(C_6H_5)_2PH]_2.H_2PtCl_6$, which is a yellow powder. On reaction with diphenylchlorophosphine the phosphine gives tetraphenyldiphosphine, $(C_6H_5)_2P=P(C_6H_5)_2$.

Dibenzylphosphine,[2]



is obtained as a by-product in the preparation of benzylphosphine (p. 49). It crystallises in white, starry or bushy needles, M.pt. 205° C., which are odourless, tasteless, and readily soluble in boiling alcohol, but insoluble in water or acids. It does not exhibit the power shown by the secondary amines of combining with acids.

Compounds of the Type R_3P.

Five types of tertiary aromatic phosphines are described in the following pages : Ar_3P, $ArAr_2'P$, $AlkAr_2P$, Alk_2ArP, $AlkArAr'P$. As in the case of the corresponding arsenical compounds the principal methods of preparing the type Ar_3P are by application of the Fittig and Grignard reactions.

Type Ar_3P.

$$(1)\quad 3RX + PX_3 + 6Na = R_3P + 6NaX$$
$$(2)\quad 2RX + RPX_2 + 4Na = R_3P + 4NaX$$
$$(3)\quad 3MgRX + PX_3 = R_3P + 3MgX_2$$

Equation (2) is really a variation of (1), the phosphorus trihalide being replaced by an aryldichlorophosphine.

The method of preparation of mixed tertiary phosphines is indicated by the following equations :

Type $ArAr_2'P$.

$$(1)\quad RPX_2 + 2R'X + 4Na = RR_2'P + 4NaX$$
$$(2)\quad RPX_2 + 2R'X + 2Zn = RR_2'P.ZnX_2 + ZnX_2$$

Equation (2) is only applicable to phenyldibenzylphosphine.

[1] Michaelis and Gleichmann, *Ber.*, 1882, 15, 801; Dörken, *Ber.*, 1888, 21, 1505.
[2] Hofmann, *Ber.*, 1872, 5, 100.

Type $AlkAr_2P$.

(1) $2Ar_2PX + ZnAlk_2 = 2Ar_2AlkP + ZnX_2$

(2) $(C_2H_5)_2(C_6H_5.CH_2)_2PCl = (C_2H_5)(C_6H_5.CH_2)_2P.HCl + C_2H_4$

Equation (2) shows a special case in which the decomposition is brought about by heat. A similar case is given in equation (2) below.

Type Alk_2ArP.

(1) $ArPX_2 + ZnAlk_2 = Alk_2ArP + ZnX_2$

(2) $(C_2H_5)_3(C_6H_5.CH_2)PCl = (C_2H_5)_2(C_6H_5.CH_2)P.HCl + C_2H_4$

(3) $ArPX_2 + 2AlkMgX = Alk_2ArP + 2MgX_2$

Type AlkArAr′P.

(1) $AlkMgX + ArAr'PX = AlkArAr'P + MgX_2$

(2) $2ArAr'PX + ZnAlk_2 = 2AlkArAr'P + ZnX_2$

All the compounds of the types Ar_3P and $ArAr_2'P$ may be isolated in the solid state. Some of them yield mercurichlorides and platinichlorides, but in no cases are compounds formed with carbon disulphide, a fact which distinguishes aliphatic and aromatic tertiary phosphines. In contra-distinction to the corresponding arsenical compounds they do not yield stable dihalides of the type R_3PX_2. The halogen probably forms a weak linkage with the phosphorus, since the greenish syrup obtained by chlorinating triphenylphosphine yields a dihydroxide, $(C_6H_5)_3P(OH)_2$, on treatment with sodium hydroxide, whilst heating alone causes it to decompose into chlorobenzene and diphenylchlorophosphine. The compounds do not combine with alkyl iodides so readily as the tertiary aromatic arsines, and phenyldibenzylphosphine does not combine at all with alkyl iodides or benzyl chloride. The products containing both aliphatic and aromatic radicals show some properties reminiscent of the purely aliphatic phosphines. The compounds $AlkAr_2P$ are all oils of pungent odour which undergo oxidation to the corresponding oxides. Increase in the aliphatic radicals, as in type Alk_2ArP, again introduces the properties of combination with carbon disulphide, ready addition of alkyl iodides, and the formation of platinichlorides and mercurichlorides. The compounds Alk_2ArP are all liquids, likewise those of the type AlkArAr′P, many of them having intolerable odours.

Compounds of the Type Ar_3P.

Triphenylphosphine,

may be obtained in several ways: (1) Chlorobenzene, 200 grams, or the corresponding amount of bromobenzene, is treated with 90 grams of phosphorus trichloride in 5 parts of dry ether, 50 grams of finely sliced sodium are added and the whole heated under reflux on the water-bath for 24 hours. A further 100 grams of sodium are then added and the heating continued for a further period of 24 hours. After filtering and washing the residue with ether, the solvent is removed from the filtrate, the residual oil solidifying on trituration with alcohol.

Purification may be effected by recrystallisation from ether-alcohol, the product melting at 79° C. The yield is about 30 per cent. Various by-products are produced in this preparation, the use of larger quantities of phosphorus trichloride appearing to increase the quantity of by-product.[1] (2) Instead of using phosphorus trichloride as in the foregoing method, it may be replaced by phenyldichlorophosphine, the reaction requiring 6 to 10 days for completion at the ordinary temperature and taking place according to the equation [2]

$$C_6H_5.PCl_2 + 2C_6H_5Br + 4Na = (C_6H_5)_3P + 2NaCl + 2NaBr$$

(3) To a solution of magnesium phenyl bromide (from 5·2 grams of magnesium, 34·1 grams of bromobenzene and 108 c.c. of absolute ether, prepared in an atmosphere of hydrogen) is added slowly, during fifteen to twenty minutes, with good cooling and shaking, a solution of 6 grams of phosphorus trichloride in 35 c.c. of absolute ether, the operation being conducted in a hydrogen atmosphere. The reaction product is decomposed with 80 c.c. of water and 11 c.c. of concentrated hydrochloric acid. The ether layer is removed and distilled, when 0·7 gram of diphenyl is obtained and the residue not distillable at 285° C. is crude triphenylphosphine.[3] Two crystallisations from alcohol give 8·7 grams (76 per cent.) of snow-white needles, M.pt. 79·5° C.[4]

Triphenylphosphine crystallises in large transparent prisms or tablets belonging to the monosymmetric system, readily soluble in most organic solvents, with the exception of alcohol. The following physical constants have been determined : density, 1·194 ; refractive index,[5] n_D, 156·75 at 4·8° to 6·9° C. ; heat of formation, 382,200 calories ; heat of combustion at constant pressure, 2,480,700 calories.[6] In an inert gas stream it distils unchanged above 360° C. It only possesses feeble basic properties. In concentrated sulphuric acid it forms a clear solution, but with the fuming acid a sulphonic acid is obtained. The solution in fuming hydrochloric acid yields the phosphine unchanged on treatment with water. Hydriodic acid (density 1·56) reacts with the phosphine, forming triphenylphosphonium iodide, which is insoluble in cold hydriodic acid, but decomposed by water. Dry chlorine reacts violently with triphenylphosphine, forming a greenish-yellow syrup, transformed by sodium hydroxide into triphenylphosphine dihydroxide. The syrup, when heated, is decomposed into chlorobenzene and diphenylchlorophosphine. It is noticeable that no dichloride is formed by treatment with chlorine, and a similar result is noted when the phosphine is heated with phosphorus trichloride at 290° to 310° C. The products obtained by the action of bromine or iodine are also easily oxidised. The phosphine does not react when heated with cold carbon disulphide, this forming a distinction between aromatic and

[1] Michaelis and Soden, *Annalen*, 1885, **229**, 295; *Ber.*, 1884, **17**, 921; compare Michaelis and Reese, *Ber.*, 1882, **15**, 1610.

[2] Michaelis and Gleichmann, *Ber.*, 1882, **15**, 801.

[3] The products of reaction between magnesium phenyl bromide and phosphorus pentachloride in ether are diphenyl, triphenylphosphine, triphenylphosphine dihydroxide, tetraphenylphosphonium bromide, $(C_6H_5)_4PBr.2H_2O$, M.pt. 286° to 288° C., and a crystalline complex, $C_6H_5MgBr.MgBr_2.MgCl_2.4(C_2H_5)_2O$.

[4] Dodonov and Medox, *Ber.*, 1928, **61**, [B], 907; compare Pfeiffer, *Ber.*, 1904, **37**, 4620.

[5] Zecchini, *Gazzetta*, 1894, **24**, i, 34.

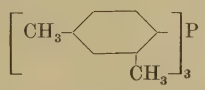
[6] Lemoult, *Compt. rend.*, 1909, **149**, 554.

aliphatic tertiary phosphines. Sulphur in carbon disulphide solution gives triphenylphosphine sulphide. The *triphenylphosphonium iodide* already mentioned crystallises in needles, M.pt. 215° C., and methyl iodide, methylene iodide and ethylene bromide when treated with the phosphine yield respectively triphenylmethylphosphonium iodide, methylene hexaphenylphosphonium iodide and ethylene hexaphenylphosphonium bromide. *Mercuric chloride* and the phosphine form a *double compound*, crystallising in needles, M.pt. above 300° C.,[1] and platinic chloride gives a pale yellow, amorphous *platinichloride*. Triphenylphosphine forms *additive compounds* with *antimony*, *arsenic* and *bismuth trichlorides*, which melt at 96° C., 100° C. and 100° to 105° C. respectively.[2] Phosphorus trichloride under similar conditions does not give a double compound. Under a constant pressure of 60 atmospheres of hydrogen, triphenylphosphine decomposes at 350° C., but under similar conditions separation of phosphorus does not take place in an atmosphere of nitrogen.[3]

Tri-p-tolylphosphine,[4]

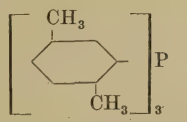
is produced in a similar manner to the phenyl compound. It separates from alcohol in white prisms, M.pt. 146° C. These form compounds of types resembling those given by triphenylphosphine. Nitration with "mixed acid" gives a *trinitro-derivative*, consisting of fine yellow needles, M.pt. 153° C., the corresponding *triamino-compound* melting at 235° C. It crystallises with one molecule of alcohol and forms an orange *platinichloride*.

Tri-m-xylylphosphine,



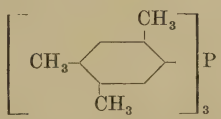
forms white, glistening needles, M.pt. 154° C., soluble in the usual organic solvents. It yields a *mercurichloride*, M.pt. 270° C.

Tri-p-xylylphosphine,



crystallises from hot acetic acid in white needles, M.pt. 155° C.; it yields a *mercurichloride*, M.pt. 256° C.

Tripseudocumylphosphine,



[1] The double compound of triphenylphosphine and mercuric chloride has the composition $[(C_6H_5)_3P]_2.HgCl_2$, not $(C_6H_5)_3P.HgCl_2$ (Kolitowska, *Rocz. Chem.*, 1928, 8, 568).

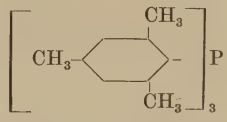
[2] Challenger and Pritchard, *Trans. Chem. Soc.*, 1924, 125, 864.

[3] Ipatiev and Razubaiev, *Ber.*, 1930, 63, [B], 1110.

[4] Michaelis, *Annalen*, 1901, 315, 78; Ohm, *Inaug. Dissert. Rostock*, 1891.

This is obtained in the usual manner from bromopseudocumol, but the reaction is slow. The product crystallises from petroleum ether-chloroform mixture in glistening, delicate needles, M.pt. 216° to 217° C.

Trimesitylphosphine,



is a white, crystalline powder, M.pt. 205° to 206° C., difficult to prepare and obtained only in poor yield.

Tri-biphenylphosphine,[1]

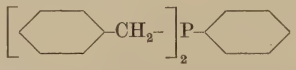
is prepared by the interaction of 4-chlorodiphenyl, phosphorus trichloride and sodium in dry benzene solution, using a crystal of antimony trichloride as a catalyst. It crystallises from benzene in slender needles, M.pt. 172° C., readily soluble in chloroform or hot glacial acetic acid.

Compounds of the Type $ArAr_2'P$.

Phenyldi-p-tolylphosphine,[2]

occurs when phenyldichlorophosphine and *p*-bromotoluene in ether solution react in the presence of sodium. The phosphine separates in small, colourless crystals, M.pt. 57° C., readily soluble in ether, sparingly soluble in alcohol.

Phenyldibenzylphosphine,[3]



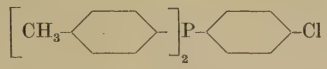
Two parts of benzyl chloride and one part of phenyldichlorophosphine are heated under reflux with granulated zinc for a short time. The reaction is violent and hydrogen chloride is evolved. When the reaction subsides the mass is mixed with ether and treated with sodium hydroxide. The *zinc chloride additive compound* separates out, is filtered off, washed with water and dissolved in alcohol. Addition of water to the solution then precipitates white flocks, which, on crystallisation from 50 per cent. acetic acid, give white needles, M.pt. 169° to 170° C., subliming at 170° to 171° C. This phosphine does not combine with alkyl iodides, and heating with benzyl chloride for 15 hours at 200° C. produces no change. It is only slowly attacked by feeble oxidising agents, but potassium dichromate converts it into benzoic and phosphoric acids; nascent hydrogen, or heating with soda lime, gives benzene, toluene and phosphoric acid.

[1] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2933.

[2] Dörken, *Ber.*, 1888, **21**, 1505.

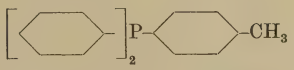
[3] Michaelis and Gleichmann, *Ber.*, 1882, **15**, 1961; Gleichmann, *Inaug. Dissert. Tübingen*, 1882.

p-Chlorophenyldi-p-tolylphosphine,[1]



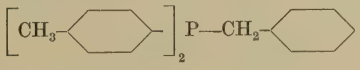
results in 37 per cent. yield when *p*-chlorophenyldichlorophosphine, *p*-bromotoluene and sodium react in benzene solution. It forms colourless, strongly refractive crystals, M.pt. 115° C., easily soluble in the usual solvents, sparingly soluble in cold water. It undergoes the customary reactions of a triarylphosphine.

Diphenyl-p-tolylphosphine,[2]



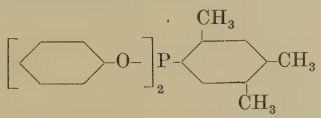
results when diphenylchlorophosphine, *p*-bromotoluene and sodium react in ether solution. It crystallises in small, colourless prisms, M.pt. 68° C., readily soluble in ether. It is a weak base, dissolving in concentrated hydrochloric acid, from which solution it may be reprecipitated by the addition of water.

Di-p-tolylbenzylphosphine,



forms colourless needles, M.pt. 187° C.

Diphenoxypseudocumylphosphine,[3]



is a thick, colourless, pungent oil, B.pt. 283° C. at 40 mm., density 1·144 at 15° C., n_D 1·5085 at 15° C. When kept for a long period it slowly forms colourless plates, M.pt. 59° C., and when boiled with water yields phenol and pseudocumylphosphinous acid.

Compounds of the Type $AlkAr_2P$.

Methyldiphenylphosphine, $CH_3(C_6H_5)_2P$, occurs when zinc dimethyl is allowed to interact with diphenylchlorophosphine.[4] It is a colourless, refractive oil, B.pt. 284° C., density 1·0784 at 15° C. It has a pungent odour, and is miscible with alcohol or benzene, but insoluble in ether. Oxidation converts it into the corresponding oxide.

Methylditolylphosphine, $CH_3(C_7H_7)_2P$, is a colourless liquid, B.pt. 345° C.

Ethyldiphenylphosphine, $C_2H_5(C_6H_5)_2P$, is obtained as a colourless, strongly refractive oil, B.pt. 203° C., having a pungent odour, and readily undergoing oxidation with formation of ethyldiphenylphosphine oxide.

Ethyldibenzylphosphine, $C_2H_5(C_6H_5.CH_2)_2P$.—This phosphine is obtained in the form of its *hydrochloride* when diethyldibenzylphos-

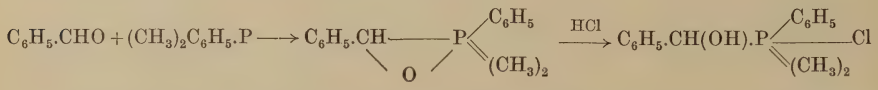
[1] Michaelis, *Annalen*, 1901, 315, 93.
[2] Dörken, *loc. cit.*
[3] Michaelis, *Annalen*, 1897, 294, 34.
[4] Michaelis and Link, *Annalen*, 1881, 207, 193.

phonium chloride is decomposed by heat.[1] It boils at 320° to 330° C., and is an oily liquid, fuming in air and possessing a pungent odour.

Compounds of the Type Alk_2ArP.

Dimethylphenylphosphine, $(CH_3)_2C_6H_5.P$.[2]—One molecular proportion of zinc dimethyl in a large volume of benzene is treated with one molecular proportion of phosphenyl chloride in the same solvent, the mixture being cooled in ice and the air in the apparatus being replaced by carbon dioxide. The reaction takes place smoothly and two layers separate, the lower one containing the *double compound* of the base with *zinc chloride*. This layer is separated, the benzene removed, and the residue treated with sodium carbonate, then with solid potassium hydroxide several times.

The phosphine is a colourless, strongly refractive liquid, B.pt. 192° C. at 11 mm., density 0·9768, possessing a pungent fishy odour. Exposure to the air causes oxidation to the oxide. The base unites with dry hydrogen chloride, giving a solid *monohydrochloride* and a liquid *dihydrochloride*. The *platinichloride* crystallises in orange plates. When phosphenyl chloride is added dropwise to dimethylphenylphosphine, heat is evolved and a solid obtained which appears to be phenyldichlorophosphine. Dimethylphenylphosphine and *carbon disulphide* react in ether solution to form an *addition compound*, $(CH_3)_2C_6H_5.P.CS_2$, which crystallises in red scales, melting in an open tube at 97° C. with dissociation, and in a closed tube at 101° C.; dry hydrogen chloride or methyl iodide causes elimination of the carbon disulphide and the formation of phosphonium compounds, whilst water tends to cause slow decomposition at ordinary temperatures. The double compound has basic properties and yields a pale yellow, amorphous *platinichloride*, $[(CH_3)_2C_6H_5.P.CS_2.HCl]_2PtCl_4$, which slowly loses carbon disulphide on exposure to the air. Combination between dimethylphenylphosphine and *benzal chloride* gives a deliquescent *compound* which forms a pale yellow *platinichloride*, M.pt. 50° C., having the composition $[HO.CH.C_6H_5(CH_3)_2P(C_6H_5)Cl]_2PtCl_4$. The same substance also occurs if the benzal chloride is replaced by benzaldehyde and the mixture heated to 100° C. in the presence of aluminium chloride. The course of the reaction is represented as follows :



Dimethyl-p-tolylphosphine, $(CH_3)_2C_7H_7.P$, isolated in a similar manner to the foregoing phosphine, is a colourless, pungent liquid, B.pt. 210° C., which is not oxidised in air, but yields dimethyl-*p*-tolylphosphine oxide on treatment with mercuric oxide. It reacts violently with methyl iodide to form the corresponding phosphonium compound. *Benzyl chloride* forms a non-crystalline *product* with the phosphine, this substance forming a *platinichloride*, M.pt. 226° C. The phosphine gives a *carbon disulphide compound*, yielding clear red plates, M.pt. 110° C. in an open tube, 116° C. in a closed tube.

[1] Collie, *Trans. Chem. Soc.*, 1888, 53, 714, 720.

[2] Michaelis and Ananoff, *Ber.*, 1875, 8, 493; Michaelis, *Annalen*, 1876, 181, 265; Kohler and Michaelis, *Ber.*, 1877, 10, 807; Czimatis, *ibid.*, 1882, 15, 2014; Holle, *ibid.*, 1892, 25, 1518.

Dimethyl-m-xylylphosphine, $(CH_3)_2C_8H_9.P$.—This compound was first described as a colourless liquid, B.pt. 230° C.[1] Further investigation[2] produced a liquid of B.pt. 233° C. It is difficult to know whether the latter product was pure, since the starting material was *m*-xylyldichlorophosphine, M.pt. 256° C., isolated from a mixture of the 1 : 3 : 4- and 1 : 3 : 5-isomers. The phosphine forms a *double compound* with *carbon disulphide* which crystallises in red needles or plates, M.pt. 115° C., and also a *methiodide* capable of existing in two isomeric forms.

Diethylphenylphosphine, $(C_2H_5)_2C_6H_5.P$, is prepared in a similar manner to the corresponding dimethyl compound.[3] It is a colourless liquid, having a pungent odour and boiling at 221·9° C.; density 0·9571 at 13° C. It is not readily oxidised in air, but detonates when warmed in pure oxygen, carbon separating out. It inflames in contact with chlorine, but if the latter is diluted with air the normal dichloride is formed. Dry hydrogen chloride reacts to form a *dihydrochloride*, which on distillation decomposes to the free base and probably a *monohydrochloride*. The latter is deliquescent in air and insoluble in ether; its aqueous solution with platinic chloride gives a yellow crystalline *platinichloride*, $[(C_2H_5)_2C_6H_5.P.HCl]_2PtCl_4$, melting at 100° C. to a resinous mass. Combination between the phosphine and methyl iodide takes place with explosive violence, but reaction with *carbon disulphide* is slow, a red *product* resulting; no compound is isolated by the action of benzaldehyde.[4] In the undiluted state the phosphine reacts explosively with *phenyl azide*, but in ether solution a crystalline *compound* results.[5] The base will dissolve sulphur when added in small quantities and the mixture gently warmed, the *sulphide*, $(C_2H_5)_2C_6H_5.PS$, probably being formed.

Diethylbenzylphosphine, $(C_2H_5)_2(C_6H_5CH_2)P$, occurs in the form of its hydrochloride when triethylbenzylphosphonium chloride is heated above 300° C. The *hydrochloride* boils at 325° to 330° C., and is converted into the free phosphine by sodium hydroxide. The base boils at 250° to 255° C.,[6] fumes in air, and is easily oxidised. Nitric acid converts it into the oxide.

Diethyl-o-tolylphosphine, $(C_2H_5)_2C_7H_7.P$, is a colourless liquid, B.pt. 263° C., and possessing an unpleasant odour.[7]

Diethyl-p-tolylphosphine, $(C_2H_5)_2C_7H_7.P$, boils at 240° C.

Diethyl(ethylphenyl)phosphine, $(C_2H_5)_2(C_6H_4.C_2H_5)P$, is a colourless liquid, B.pt. 268° to 270° C., density 0·929 at 17° C.

Diethylanisylphosphine, $(C_2H_5)_2(C_6H_4.OCH_3)P$, is isolated as a colourless liquid, possessing an intensely pungent odour. It boils at 266° to 267° C., and has a density of 0·9978 at 18° C. The *platinichloride* separates in pale yellow columns, M.pt. 103° C.

Diethylphenetylphosphine, $(C_2H_5)_2(C_6H_4.OC_2H_5)P$, boils at 275° C.

Diethylchlorophenylphosphine, $(C_2H_5)_2(C_6H_4Cl)P$, is a colourless liquid which soon becomes yellow. It boils at 255° to 257° C., and has an unpleasant odour.

[1] Czimatis, *loc. cit.*
[2] Conen, *Ber.*, 1898, **31**, 2919.
[3] Michaelis and Ananoff, *loc. cit.*; Michaelis, *Annalen*, 1876, **181**, 345.
[4] Czimatis, *loc. cit.*; Holle, *loc. cit.*
[5] Staudinger and Meyer, *Helv. Chim. Acta*, 1919, [ii], 619.
[6] Collie, *Trans. Chem. Soc.*, 1881, **53**, 714, 720.
[7] Michaelis, *Annalen*, 1896, **293**, 235.

Diethylbromophenylphosphine, $(C_2H_5)_2(C_6H_4Br)P$, is a colourless liquid boiling at 265° C. It has a vile odour, and yields a pale yellow *platinichloride.*

Diethylxylylphosphine, $(C_2H_5)_2C_8H_9.P$, is a colourless liquid, B.pt. 260° C.

Diethylpseudocumylphosphine, $(C_2H_5)_2C_9H_{11}.P$, is a pungent liquid, boiling at 274° to 275° C., not oxidised in air. Its *platinichloride* separates as red crystals.[1]

Diethoxypseudocumylphosphine, $(C_2H_5O)_2C_9H_{11}.P$, boils at 232° to 233° C. at 100 mm., density 1·048 at 15° C., n_D 1·505.

Diethylmesitylphosphine, $(C_2H_5)_2C_9H_{11}.P$, is a clear liquid, B.pt. 170° C., having an unpleasant odour, and not oxidised in air. Its *platinichloride,* $(C_2H_5)_2C_9H_{11}.P.H_2PtCl_6$, crystallises from dilute alcohol as shining orange-yellow crystals.

Diethylcymylphosphine, $(C_2H_5)_2C_{10}H_{13}.P$, boils at 260° to 270° C.

Diethyl-α-naphthylphosphine, $(C_2H_5)_2C_{10}H_7.P$, is obtained by the interaction of α-naphthyldichlorophosphine and zinc diethyl, the operation being conducted in cooled benzene and the reaction completed by boiling.[2] It is a pungent, yellow oil, B.pt. 360° C. with partial decomposition. It behaves towards hydrogen chloride, oxygen and sulphur in a similar manner to the corresponding phenyl compound, but the reactions are less vigorous.

Di-n-propylphenylphosphine, $(C_3H_7)_2C_6H_5.P$, occurs when 19 c.c. of phenyldichlorophosphine are added to the magnesium *n*-propyl bromide obtained from 36 c.c. of *n*-propyl bromide and 10 grams of magnesium. The yield is 17 grams. The product boils at 159° C. at 50 mm., and has a density of 0·925 at 25° C.[3] The *mercurichloride* separates from alcohol as needles, M.pt. 192·5° C.

Di-n-propyltolylphosphine, $(C_3H_7)_2C_7H_7.P$, boils at 174° C. at 50 mm.; its density is 0·921 at 25° C. The *mercurichloride* crystallises from glacial acetic acid as prisms, M.pt. 129·5° C.

Di-n-butylphenylphosphine, $(C_4H_9)_2C_6H_5.P$, is a colourless liquid, B.pt. 184·5 to 185·5° C. at 50 mm., density 0·9115 at 25° C. Its *mercurichloride* separates from alcohol in fine needles, M.pt. 160·5° C.[4]

Di-n-butyl-p-tolylphosphine, $(C_4H_9)_2C_7H_7.P$, prepared in the usual manner, boils at 197° C. at 50 mm., density 0·9076. The *mercurichloride* is isolated from alcohol as prisms, M.pt. 112° C.

Di-isobutylphenylphosphine, $(C_4H_9)_2C_6H_5.P$.—Phenyldichlorophosphine, 11 c.c., is added to the Grignard reagent from 47 c.c. of *iso*butyl bromide and 10 grams of magnesium, the yield of phosphine being 10 grams.[5] It boils at 168° C. at 50 mm., and has a density of 0·910 at 25° C. The *mercurichloride* yields white needles, melting at 158·5° C. to a cloudy liquid.

Di-isobutyl-p-tolylphosphine, $(C_4H_9)_2C_7H_7.P$, prepared in a similar manner to the previous phosphine, boils at 182·5° to 184·5° C. at 50 mm., density 0·915 at 25° C. The yield of *mercurichloride* is small, and the product which crystallises from alcohol in cubic crystals does not appear to be pure.

Di-n-amylphenylphosphine, $(C_5H_{11})_2C_6H_5.P$.—Phenyldichloro-

[1] Michaelis, *Annalen,* 1897, 294, 34. [2] Kelbe, *Ber.,* 1878, 11, 1499.
[3] Davies, Pearse and Jones, *J. Chem. Soc.,* 1929, p. 1262.
[4] Davies and Jones, *J. Chem. Soc.,* 1929, p. 33.
[5] Davies, Pearse and Jones, *loc. cit.*

phosphine (11·5 c.c.) is added to the Grignard solution from 42 c.c. of *n*-amyl bromide and 8 grams of magnesium. The yield is 10 grams, the product boiling at 210° C. at 50 mm., and having a density of 0·902 at 25° C. The phosphine is only partially miscible with absolute ethyl alcohol at 15° C. The *mercurichloride* crystallises well from alcohol and melts at 108° C.

Di-n-amyl-p-tolylphosphine, $(C_5H_{11})_2C_7H_7.P$, boils at 220° C. at 50 mm., and has a density of 0·898 at 25° C. It is still less miscible with absolute ethyl alcohol than the corresponding phenylphosphine. The *mercurichloride* crystallises well from glacial acetic acid and melts at 112° C.

Di-isoamylphenylphosphine, $(C_5H_{11})_2C_6H_5.P$, prepared in the usual manner, boils at 198·5° C. at 50 mm., and has a density of 0·900 at 25° C. The *mercurichloride* crystallises in needles which melt to a cloudy liquid at 152° C.

Di-isoamyl-p-tolylphosphine, $(C_5H_{11})_2C_7H_7.P$, boils at 210° C. at 50 mm., density 0·894 at 25° C. It is only partially miscible with ethyl alcohol at 15° C. It forms a *mercurichloride* which separates from glacial acetic acid in prisms, M.pt. 107° C.

Di(dl-β-methylbutyl)phenylphosphine, $(CH_3.C_4H_8)_2C_6H_5.P$, is obtained by adding 14 c.c. of phenyldichlorophosphine to the magnesium *dl*-β-methylbutyl bromide from 51 c.c. of the bromide and 10 grams of magnesium. The yield is 8 grams, and the product boils at 198° C. at 50 mm., density 0·906 at 25° C. The *mercurichloride* melts at 120° C.

Di(dl - β - methylbutyl)p-tolylphosphine, $(CH_3.C_4H_8)_2C_7H_7.P$, boils at 210° to 211° C. at 50 mm., and has a density of 0·902 at 25° C. The *mercurichloride*, prepared in the usual manner, melts at 99° C.

Di(δ - methylamyl)phenylphosphine or **Di-isohexylphenylphosphine,** $(C_6H_{13})_2C_6H_5.P$.—A solution of 13 c.c. of phenyldichlorophosphine in 100 c.c. of ether is introduced into the Grignard reagent prepared from 60 c.c. of δ-methylamyl bromide, 10 grams of magnesium and 350 c.c. of ether. The yield is 7 grams, and the product boils at 219° C. at 50 mm.

Di(δ-methylamyl)p-tolylphosphine, $(C_6H_{13})_2C_7H_7.P$, boils at 234° to 235° C. at 50 mm., has a density of 0·888 at 25° C., and gives a *mercurichloride*, M.pt. 110·5° C., which crystallises from glacial acetic acid in prisms.

Di-n-propyl-p-anisylphosphine,[1] $(C_3H_7)_2(C_6H_4.OCH_3)P$, boils at 165° C. at 17 mm.; density 0·9738 at 25° C.; n_F 1·5477 at 25° C., $[R_L]_F$ 73·08; n_D 1·5352 at 25° C., $[R_L]_D$ 71·69; n_C 1·5301 at 25° C., $[R_L]_C$ 71·12. Its ether solution yields a *dibromide* in the form of a viscous oil, and the *mercurichloride*, $C_{13}H_{21}OP.HgCl_2$, separates from glacial acetic acid in prismatic crystals, M.pt. 134° C.

Di-n-butyl-p-anisylphosphine, $(C_4H_9)_2(C_6H_4.OCH_3)P$, boils at 190° C. at 16 mm.; density 0·9600 at 25° C.; n_F 1·5389 at 25° C., $[R_L]_F$ 82·28; n_D 1·5274 at 25° C., $[R_L]_D$ 80·82; n_C 1·5226 at 25° C., $[R_L]_C$ 80·20.

Di-n-amyl-p-anisylphosphine, $(C_5H_{11})_2(C_6H_4.OCH_3)P$, boils at 202° C. at 18 mm.; density 0·9382 at 25° C.; n_F 1·5289 at 25° C., $[R_L]_F$ 92·10; n_D 1·5178 at 25° C., $[R_L]_D$ 90·48; n_C 1·5132 at 25° C., $[R_L]_C$ 89·80. The *mercurichloride* forms elongated plates, M.pt. 114° C., and the *dibromide* melts at about 85° C.

[1] Jackson, Davies and Jones, *J. Chem. Soc.*, 1930, p. 2298.

Di-n-propyl(p-ethylphenyl)phosphine, $(C_3H_7)_2(C_6H_4.C_2H_5)P$,[1] boils at 157° C. at 21 mm.; density 0·9147 at 25° C.; n_F 1·5370 at 25° C., $[R_L]_F$ 75·86; n_D 1·5255 at 25° C., $[R_L]_D$ 74·50; n_C 1·5208 at 25° C., $[R_L]_C$ 73·94. Bromine in ether solution gives an oily *dibromide.*

Di-n-butyl(p-ethylphenyl)phosphine, $(C_4H_9)_2(C_6H_4.C_2H_5)P$, boils at 176° C. at 15 mm.; density 0·9042 at 25° C.; n_F 1·5319 at 25° C., $[R_L]_F$ 85·74; n_D 1·5208 at 25° C., $[R_L]_D$ 84·24; n_C 1·5162 at 25° C., $[R_L]_C$ 83·61. The *dibromide* is a viscous liquid.

Di-n-amyl(p-ethylphenyl)phosphine, $(C_5H_{11})_2(C_6H_4.C_2H_5)P$, boils at 201° C. at 18 mm.; density 0·9022 at 25° C. Its *mercurichloride* forms elongated prisms, M.pt. 95° C.

Compounds of the Type AlkArAr'P.

Methylphenyl-p-tolylphosphine, $(CH_3)(C_6H_5)(C_7H_7)P$, occurs when phenyl-*p*-tolylchlorophosphine reacts with magnesium methyl iodide, the best proportions being four molecular proportions of Grignard reagent to one of secondary phosphine.[2]

Ethylphenyl-p-tolylphosphine, $(C_2H_5)(C_6H_5)(C_7H_7)P$, may be isolated by treating phenyl-p-tolylchlorophosphine with zinc diethyl or magnesium ethyl bromide.[3] It has an intolerable odour, boils at 340° C., and is readily soluble in concentrated hydrochloric acid. It yields a *platinichloride* which crystallises in pale yellow needles.

Ethylphenylpseudocumylphosphine, $(C_2H_5)(C_6H_5)(C_9H_{11})P$, is a pale yellow viscous oil of unpleasant odour.[4] It boils normally at 352° C. or at 225° to 230° C. at 10 mm. It forms a *mercurichloride* and a *platinichloride.*

Compounds of the Type R_4PX (Phosphonium Compounds).

The following eight types of compounds are included under the general formula R_4PX: Ar_4PX, $AlkAr_3PX$, Alk_2Ar_2PX, $AlkAlk'Ar_2PX$, Alk_3ArPX, $Alk_2Alk'ArPX$, $AlkAlk'ArAr'PX$, $(ArO)_3AlkPX$, and compounds represented by such formulæ as $C_6H_5.P(NC_5H_{10})_2(CH_3)I$ and $(C_9H_{10}N)_3P(CH_3)I$. It should be noted that the phosphines corresponding to the last three formulæ would not be considered to be organometallic from the point of view of this volume since they contain phosphorus directly linked to oxygen or nitrogen, but when the phosphorus becomes pentavalent, with the formation of a phosphonium compound, a link is made with a carbon atom, necessitating inclusion in this book.

The general equation for the preparation of phosphonium compounds of the type Alk_2Ar_2PX is

$$AlkAr_2P + AlkX = Alk_2Ar_2PX$$

All the compounds Alk_2Ar_2PX are solids of high melting-point and yield platinichlorides, yellowish-red crystalline substances. Similar remarks apply to the type $AlkAlk'Ar_2PX$.

The trialkyl compounds, Alk_3ArPX, are obtained from dialkylarylphosphines and alkyl halides:

$$Alk_2ArP + AlkX = Alk_3ArPX$$

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[1] Jackson, Davies and Jones, *loc. cit.*

[2] Radcliffe and Brindley, *Chemistry and Industry*, 1923, 42, 64.

[3] Michaelis, *Annalen*, 1901, 315, 60; Wedekind, *Ber.*, 1912, 45, 2933.

[4] Michaelis, *loc. cit.*

They usually crystallise in needles and yield platinichlorides. Silver oxide reacts with aqueous solutions of the iodides giving deliquescent hydroxides.

Mixed trialkyl derivatives, $Alk_2Alk'ArPX$, are formed by treating dialkylarylphosphines with alkyl halides containing a different radical to the phosphine :

$$Alk_2ArP + Alk'X = Alk_2Alk'ArPX$$

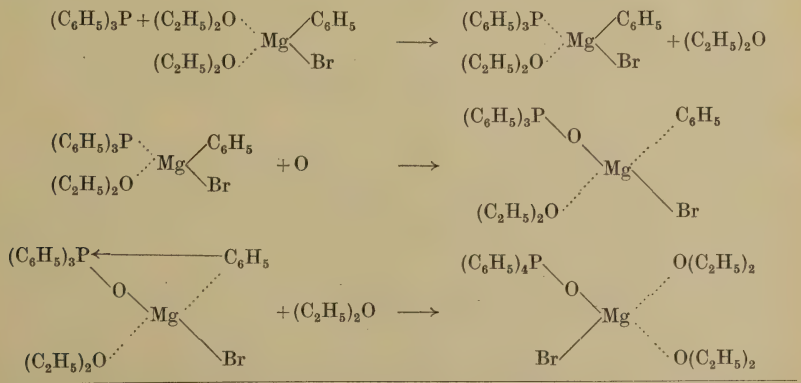
All are well-defined crystalline products, the platinichlorides being known in some cases.

The compounds $AlkAlk'ArAr'PX$ occur when the type $AlkArAr'P$ is used as the starting-point and treated with an alkyl halide.

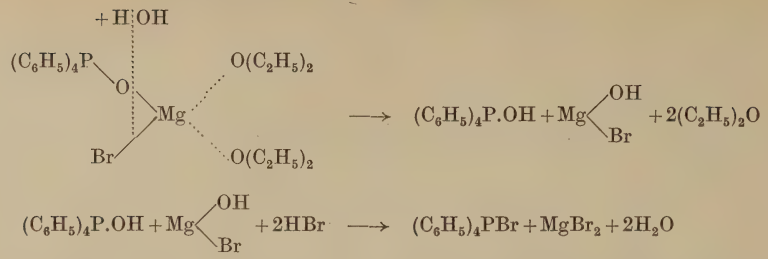
The preparation of the aryloxy-derivatives and the N-phosphonium compounds consists in direct addition of the alkyl halides to the phosphines.

Compounds of the Type Ar_4PX.

Tetraphenylphosphonium bromide, $(C_6H_5)_4PBr$.[1]—Four grams of triphenylphosphine in 8 c.c. of absolute ether are added to the Grignard solution from 1·48 grams of magnesium and 9·56 grams of bromobenzene in 60 c.c. of absolute ether, the reaction being carried out in an atmosphere of hydrogen. The whole is then cooled in ice and a stream of dry oxygen passed in for ninety minutes, the mixture being well shaken. Hydrobromic acid (9·5 c.c. of 48 per cent. acid and 20·5 c.c. of water) is then gradually added to the cooled solution, which is continually agitated, two layers separating in the reaction flask. The aqueous bottom layer yields a copious crystalline precipitate ; the upper ether layer is separated and extracted three times with more ether. The crystals dissolve on warming in the aqueous mother liquors and separate on cooling as pale yellow needles. The yield is 4·65 grams or 72·7 per cent. Purification is effected by solution in alcohol and recrystallisation. The product melts at 281° to 284° C. Crystallisation from water gives colourless needles, $(C_6H_5)_4PBr.2H_2O$, the water being eliminated *in vacuo* and the water-free compound melting at 287° C. The compound is very soluble in alcohol or chloroform, readily soluble in hot water but sparingly in cold water, insoluble in benzene or ether. The above reaction is regarded as taking place in five stages, as follows :



[1] Dodonov and Medox, *Ber.*, 1928, **61**, [B], 907.



The bromide also occurs amongst other products when phenyl magnesium bromide reacts with phosphorus pentachloride.[1]

When the bromide in aqueous solution is digested for several hours with freshly precipitated silver oxide it yields a strongly alkaline solution of *tetraphenylphosphonium hydroxide*, which readily loses benzene when concentrated even in a vacuum, yielding a residue of triphenylphosphine oxide, M.pt. 154·5° to 155° C., and tetraphenylphosphonium carbonate. Treatment of an aqueous solution of the hydroxide with hydrochloric acid gives *tetraphenylphosphonium chloride*, separating from water in large glistening needles containing five molecules of water of crystallisation; the water-free salt melts at 265° C. In a similar manner a *normal sulphate* is obtained which has eighteen molecules of water, the anhydrous salt having no definite melting-point. The corresponding *nitrate* melts with decomposition at 284° C., and the *iodide* melts at 333° C.

Tetrabenzylphosphonium iodide, $(C_6H_5.CH_2)_4PI$, occurs when one part of phosphonium iodide and two parts of benzyl alcohol are heated together for six to eight hours in a sealed tube at 100° C.[2] It forms white crystals, M.pt. 191° C., readily soluble in chloroform, ether or alcohol, becoming slightly yellow on exposure to the air. This iodide may be transformed in the usual manner into the *chloride*, *bromide*, *sulphate* or *nitrate*, all of which form white, shining crystals. *Double salts* are obtained with *platinic chloride*, and *auric*, *mercuric* and *stannic chlorides*. A *picrate* is known.

Compounds of the Type $AlkAr_3PX$.

Methyltriphenylphosphonium iodide,[3] $(CH_3)(C_6H_5)_3PI$.—Triphenylphosphine combines violently with methyl iodide to yield the phosphonium iodide, which consists of shining plates, M.pt. 165° to 166° C. The corresponding *chloride* crystallises with one molecule of water, which is eliminated at 100° to 110° C., the anhydrous compound melting at 212° to 213° C.; its *platinichloride* forms orange needles, M.pt. 237° to 238° C.

Ethyltriphenylphosphonium iodide forms broad, colourless plates, M.pt. 164° to 165° C. The *n-propylphosphonium iodide* melts at 201·5° C.; the *isopropylphosphonium iodide* yields prisms, M.pt. 191° C.; the *isobutylphosphonium iodide* separates in plates or needles, M.pt. 176° to 177° C.; and the *isoamylphosphonium iodide* crystallises in colourless prisms, M.pt. 147° C.

Methyltri-p-tolylphosphonium iodide, $(CH_3)(C_7H_7)_3PI$, separates from water in needles and from alcohol in columns, M.pt. 108° C. The *chloride* forms long plates containing two molecules of

[1] Kolitowska, *Rocz. Chem.*, 1928, **8**, 568.
[2] Ledermann, *Ber.*, 1888, **21**, 405.
[3] Michaelis and Gleichmann, *Ber.*, 1882, **15**, 801.

water, M.pt. 80° C. ; it yields a *platinichloride*, red needles, M.pt. 245° C. The *ethyl-*, *n-propyl-* and *isopropyl-phosphonium iodides* all crystallise in needles, and melt at 185° C., 182° C. and 184° C. respectively.

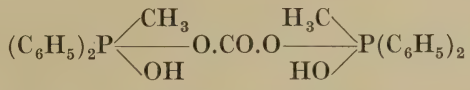
Methylene-hexaphenylphosphonium iodide, $CH_2[(C_6H_5)_3PI]_2$, occurs when methylene iodide combines with triphenylphosphine. It separates as glistening needles, becoming yellow at 190° C. and melting with decomposition at 230° to 231° C. Ethylene dibromide forms *ethylene-hexaphenylphosphonium bromide*, $C_2H_4[(C_6H_5)_3PBr]_2$, a colourless crystalline powder melting above 360° C.

Ethyltribenzylphosphonium chloride, $(C_2H_5)(C_6H_5.CH_2)_3PCl$, is obtained by heating ethyldibenzylphosphine with an excess of benzyl chloride. It is purified by crystallisation from water and the crystals contain a molecule of water of crystallisation.[1] Its decomposition on heating is not definite, but may take place according to the equations

$$(C_2H_5)(C_6H_5.CH_2)_3PCl = (C_6H_5.CH_2)_3P + C_2H_4 + HCl$$
$$2(C_2H_5)(C_6H_5.CH_2)_3PCl = 2(C_2H_5)(C_6H_5.CH_2)_2PHCl + C_{14}H_{12}$$

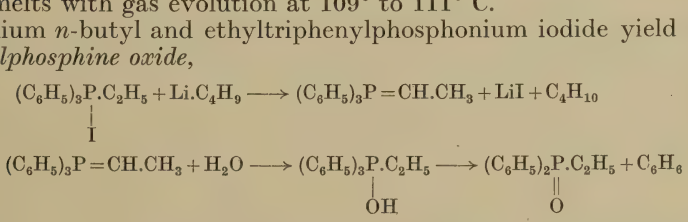
It gives a *platinichloride*, $[(C_2H_5)(C_6H_5.CH_2)_3P]_2PtCl_6$, when treated with platinic chloride. This product is insoluble in cold water, but more soluble in alcohol and hot water.

Reaction between Alkali Metal Alkyls and Phosphonium Halides.[2]—Sodium triphenylmethyl reacts in ether solution with methyltriphenylphosphonium iodide giving the *basic carbonate* of *methyldiphenylphosphine oxide*,

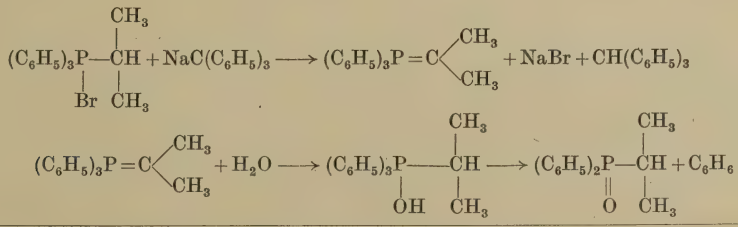


which melts with gas evolution at 109° to 111° C.

Lithium *n*-butyl and ethyltriphenylphosphonium iodide yield *ethyldiphenylphosphine oxide*,



The reaction between *iso*propyltriphenylphosphonium bromide and sodium triphenylmethyl gives a coloured solution, which in moist air becomes colourless and furnishes *isopropyldiphenylphosphine oxide*, M.pt. 142° to 143° C., the course of the reaction probably being as follows :



[1] Collie, *Trans. Chem. Soc.*, 1888, 53, 714, 720.

[2] Coffman and Marvel, *J. Amer. Chem. Soc.*, 1929, 51, 3496.

Lithium *n*-butyl and triphenyldiphenylmethylphosphonium bromide yield triphenylphosphine-diphenylmethylene, and the same product results when sodium triphenylmethyl replaces the lithium *n*-butyl.

Methyltri-m-xylylphosphonium iodide, $(CH_3)(C_8H_9)_3PI$, melts at 230·5° C. The *ethiodide* melts at 225° C., and the *platinichloride* at 252° C.

Methyltri-p-xylylphosphonium iodide, $(CH_3)(C_8H_9)_3PI$, melts at 169° C., and the corresponding *ethiodide* at 220° C.

Methyltripseudocumylphosphonium iodide, $(CH_3)(C_9H_{11})_3PI$, melts at 291° C.

Methyltrimesitylphosphonium iodide, $(CH_3)(C_9H_{11})_3PI$, is a yellow powder, M.pt. 269° C., readily soluble in water or alcohol.

Methylchlorophenyldi - p - tolylphosphonium iodide, $(CH_3)(ClC_6H_4)(CH_3.C_6H_4)_2PI$,[1] crystallises in needles, M.pt. 135° C. The corresponding *chloride* contains four molecules of water and melts at 72° C.; it gives a *platinichloride* melting with decomposition at 235° C. The *ethylphosphonium* and *benzylphosphonium compounds* melt at 176·5° C. and 257° C., respectively, the latter containing two molecules of water.

Benzyltriphenylphosphonium chloride, $(C_6H_5.CH_2)(C_6H_5)_3PCl$, obtained from triphenylphosphine and benzyl chloride, crystallises from water with one molecule of solvent. The crystals are small, white rhombs, which slake in air, melt at 287° to 288° C., and are soluble in alcohol but insoluble in ether. Treatment with concentrated potassium bromide yields the corresponding *phosphonium bromide*, small prisms, M.pt. 274° to 275° C.; the *iodide*, M.pt. 253° C., is obtained in a similar manner. The following benzyltriphenylphosphonium salts are also known: *nitrate*, glistening prisms melting with decomposition at 203° C.; *picrate*, golden-yellow needles, M.pt. 148° C.; *dichromate*, red needles decomposing at 172° to 174° C.; and *thiocyanate*, prisms, M.pt. 189° C.

Methyltri-biphenylphosphonium iodide,[2] $(CH_3)(C_6H_5.C_6H_4)_3PI$, is obtained in quantitative yield when the components are mixed. It separates from alcohol as sparkling plates melting with decomposition at 135° to 136° C.

Allyltri-biphenylphosphonium bromide, $(C_3H_5)(C_6H_5.C_6H_4)_3PBr$, forms narrow plates, M.pt. 195° to 196° C. The corresponding *benzylphosphonium compound* crystallises in plates, softening above 269° C. and melting at 277° C. The phosphonium compound from tri-biphenylphosphine and ethyl chloroacetate yields square plates, M.pt. 164° to 165° C.

Compounds of the Type Alk_2Ar_2PX.

Dimethyldiphenylphosphonium iodide, $(CH_3)_2(C_6H_5)_2PI$, occurs when methyl iodide reacts with methyldiphenylphosphine. It crystallises in needles, M.pt. 241° C., and the *platinichloride*, $[(CH_3)_2(C_6H_5)_2P]_2PtCl_6$, as yellowish-red needles, M.pt. 218° C.[3]

Diethyldiphenylphosphonium iodide, $(C_2H_5)_2(C_6H_5)_2PI$, obtained from ethyldiphenylphosphine and ethyl iodide, forms colourless

[1] Michaelis, *Annalen*, 1901, 315, 93.
[2] Worrall, *J. Amer. Chem. Soc.*, 1930, 52, 2933.
[3] Michaelis and Link, *Annalen*, 1881, 207, 193.

crystals, M.pt. 204° C., soluble in hot water but insoluble in ether. When heated in an atmosphere of carbon dioxide, ethyl iodide is not removed. The *platinichloride*, $[(C_2H_5)_2(C_6H_5)_2P]_2PtCl_6$, crystallises in yellowish-red needles, M.pt. 218° C.

Diethyldibenzylphosphonium chloride, $(C_2H_5)_2(C_6H_5.CH_2)_2PCl$, crystallises from water. Its *platinichloride* forms slender needles. Decomposition by heat takes place as follows :—[1]

$$(C_2H_5)_2(C_6H_5.CH_2)_2PCl = (C_2H_5)(C_6H_5.CH_2)_2PHCl + C_2H_4$$

Compounds of the Type $AlkAlk'Ar_2PX$.

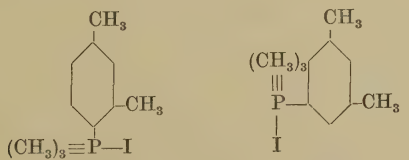
Methylethyldiphenylphosphonium iodide,[2] $(CH_3)(C_2H_5)(C_6H_5)_2PI$.—This iodide is prepared by the interaction of methyldiphenylphosphine and ethyl iodide. It forms rhombic crystals, M.pt. 181° C. A *platinichloride*, $[(CH_3)(C_2H_5)(C_6H_5)_2P]_2PtCl_6$, M.pt. 220° C., and a *picrate*, yellow needles, M.pt. 86° C., exploding when strongly heated, may be isolated from the iodide.

Compounds of the Type Alk_3ArPX.

Trimethylphenylphosphonium iodide, $(CH_3)_3C_6H_5.PI$, is isolated by the interaction of dimethylphenylphosphine and methyl iodide ; it separates as snow-white crystals, M.pt. 205° C.[3]

Trimethyl-p-tolylphosphonium iodide, $(CH_3)_3C_7H_7.PI$.—Dimethyl-*p*-tolylphosphine reacts violently with methyl iodide, forming the phosphonium compound. This consists of colourless needles, M.pt. 255° C., readily soluble in cold water, reacting with silver oxide to give a deliquescent basic mass which forms an orange-yellow *platinichloride* crystallising in plates, M.pt. 230° C. The iodide combines with iodine to form a *periodide*, $(CH_3)_3C_7H_7.PI_3$, crystallising from alcohol in steel-blue rhomboids, sparingly soluble in benzene or ether.

Trimethyl-m-xylylphosphonium iodide, $(CH_3)_3C_8H_9.PI$.—The iodide obtained by treating dimethyl-*m*-xylylphosphine with methyl iodide is capable of existing in two isomeric forms.[4] The *α-iodide* crystallises in scales or feathery needles, M.pt. 265° C., fairly soluble in water or alcohol and insoluble in ether. The *β-iodide* forms bushy needles. It is possible that these compounds have the following formulæ :—



This would mean that the dimethyl-*m*-xylylphosphine used as starting material is not pure, but a mixture of two isomers. The α-iodide forms a *hydroxide*, from which a *chloride* crystallising in white needles, M.pt. 110° C., may be isolated. A *platinichloride*, $[(CH_3)_3C_8H_9.P]_2PtCl_6$, yellow bushy needles from water, and a *gold salt*, $(CH_3)_3C_8H_9.P.AuCl_4$, long yellow needles, have also been described.

[1] Collie, *Trans. Chem. Soc.*, 1888, 53, 714.
[2] Michaelis and Link, *loc. cit.*
[3] Michaelis, *Annalen*, 1876, 181, 359.
[4] Conen, *Ber.*, 1898, 31, 2919.

Triethylphenylphosphonium iodide, $(C_2H_5)_3C_6H_5.PI$.—Diethylphenylphosphine and ethyl iodide yield this phosphonium compound in fans of needles, M.pt. 115° C., which cannot be distilled without decomposition, but are not decomposed by potassium hydroxide solution.[1] A *hydroxide* and a *platinichloride* are known, the chloride melting below 100° C.

Triethylbromophenylphosphonium iodide, $(C_2H_5)_3(C_6H_4Br)PI$, is a white crystalline compound, M.pt. 165° C.[2]

Triethyl-o-tolylphosphonium iodide, $(C_2H_5)_3C_7H_7.PI$, crystallises in colourless needles, M.pt. 162° C.

Triethylbenzylphosphonium chloride, $(C_2H_5)_3(C_6H_5.CH_2)PCl$. —This derivative is prepared by warming a large excess of benzyl chloride with triethylphosphine.[3] It crystallises from water in needles, and yields a *platinichloride*, M.pt. 78° C. When heated above 300° C. decomposition occurs according to the equation

$$(C_7H_7)(C_2H_5)_3PCl = (C_7H_7)(C_2H_5)_2PHCl + C_2H_4$$

Other phosphonium salts which may be obtained from the chloride in the usual manner are as follows, the compounds in brackets being the decomposition products formed when the salts are heated to a high temperature: *bromide* (almost totally decomposed; only resembles the chloride to a slight extent);[4] *hydroxide* (triethylphosphine oxide, toluene); *carbonate* and *acid carbonate* (triethylphosphine oxide, toluene, carbon dioxide); *sulphate* (2 mols. triethylphosphine oxide, stilbene, carbon dioxide); *acetate* (triethylphosphine oxide and methyl tolyl ketone, and to a smaller extent triethylphosphine and the methyl ester of toluic acid); *oxalate* (triethylphosphine oxide, toluene, carbon monoxide, carbon dioxide).

Triethylanisylphosphonium iodide, $(C_2H_5)_3(C_6H_4.OCH_3)PI$, occurs as long colourless needles, M.pt. 65° C.; the *platinichloride* melts at 148° C.

Triethyl-m-xylylphosphonium iodide, $(C_2H_5)_3C_8H_9.PI$, is a white crystalline powder, M.pt. 136° C.

Tri-n-propylphenylphosphonium bromide, $(C_3H_7)_3C_6H_5.PBr$, melts at 131·5° C.[5]

Tri-n-propyl-p-tolylphosphonium bromide, $(C_3H_7)_3C_7H_7.PBr$, is obtained only with difficulty when *p*-tolyldi-*n*-propylphosphine is refluxed with *n*-propyl bromide in ether solution. It forms well-developed, hygroscopic needles, M.pt. 125·5° C.

Compounds of the Type $Alk_2Alk'ArPX$.

Dimethylethylphenylphosphonium iodide, $(CH_3)_2(C_2H_5)(C_6H_5)PI$, is obtained from dimethylphenylphosphine and ethyl iodide.[6] It separates from ether solution as white crystals, M.pt. 137° C.

Dimethylbromethylphenylphosphonium bromide,[7] $(CH_3)_2(C_2H_4Br)(C_6H_5)PBr$, is produced when dimethylphenylphosphine

[1] Michaelis and Ananoff, *Ber.*, 1875, 8, 493; Michaelis, *Annalen*, 1876, 181, 345.
[2] Michaelis, *Annalen*, 1896, 293, 235.
[3] Collie, *Trans. Chem. Soc.*, 1888, 53, 714, 720; compare Hofmann, *Annalen Suppl.*, 1861, 1, 323.
[4] Collie, *Phil. Mag.*, 1887, [5], 24, 27.
[5] Davies, Pearse and Jones, *J. Chem. Soc.*, 1929, p. 1262.
[6] Michaelis and Ananoff, *loc. cit.*; Michaelis, *Annalen*, 1876, 181, 265; Kohler and Michaelis, *Ber.*, 1877, 10, 807.
[7] Gleichmann, *Ber.*, 1882, 15, 198.

(1 mol.) and ethylene dibromide (1 mol.) interact. It crystallises in colourless tablets, M.pt. 173° C., readily soluble in hot water or alcohol. Silver nitrate precipitates half the bromine as silver bromide, whilst silver oxide removes the whole of the halogen. With *platinic chloride* an orange crystalline powder is produced which has the composition $[(CH_3)_2(C_6H_5)(C_2H_4Br)PBr]_2PtCl_4$; *bromine* forms an *addition product*, $(CH_3)_2(C_6H_5)(C_2H_4Br)PBr.2Br_2$, which loses its bromine when warmed in air. On heating a concentrated alcoholic solution of the bromide with a further quantity of dimethylphenylphosphine, a crystalline precipitate of *ethylenetetramethyldiphenylphosphonium bromide* is obtained. This melts above 300° C., and gives a deep red *platinichloride*. All the bromine is removed from it by silver nitrate. Apparently it can add on five molecules of bromine, forming a red powder, soluble in glacial acetic acid with loss of bromine, a yellow *bromine addition product* separating out in needles, M.pt. 171° C., of the constitution $C_2H_4[(CH_3)_2(C_6H_5)PBr]_2Br_2$.

Diethylmethylphenylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_6H_5)PI$.[1]—Diethylphenylphosphine combines with methyl iodide with explosive violence, so that the latter must be added dropwise. The iodide melts at 95° C. and gives a *hydroxide* and *platinichloride*.

Diethylmethylchlorophenylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_6H_4Cl)PI$, is isolated as a snow-white crystalline powder, M.pt. 97° to 98° C.[2] It is derived from diethylchlorophenylphosphine and methyl iodide.

Diethylmethylbromophenylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_6H_4Br)PI$, crystallises in shining white needles, M.pt. 135° C.

Diethylmethyl-o-tolylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_7H_7)PI$.—The starting-point for the preparation of this compound is diethyl-*o*-tolylphosphine. It yields colourless needles, M.pt. 98° C.

Diethylmethyl-p-tolylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_7H_7)PI$, is obtained in colourless needles, M.pt. 137° C., and yields a *platinichloride* which crystallises in transparent yellow plates.

Diethylmethyl(ethylphenyl)phosphonium iodide, $(C_2H_5)_2(CH_3)(C_6H_4.C_2H_5)PI$, separates in needles, M.pt. 135° C. The *phenylhydrazone*, $C_8H_9P=N.NH.C_6H_5$, melts at 139° C. The *hydroxide* is only known in solution; the *platinichloride* forms yellow needles, M.pt. 195° C.[3]

Diethylmethylanisylphosphonium iodide,[4] $(C_2H_5)_2(CH_3)(C_6H_4.OCH_3)PI$, crystallises in colourless needles, M.pt. 91° C., and yields a *platinichloride*, M.pt. 142° C., which crystallises in brownish prisms.

Diethylmethylphenetylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_6H_4.OC_2H_5)PI$, is more soluble in water than the previous compound. It melts at 60° C. and the *platinichloride* crystallises in needles, M.pt. 208° C.

Diethylmethyl-m-xylylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_8H_9)PI$, is a white crystalline powder, M.pt. 90° C. The *platinichloride* derived from it forms cadmium-yellow plates, M.pt. 202° C.

[1] Michaelis and Ananoff, *Ber.*, 1875, 8, 493; Michaelis, *Annalen*, 1876, 181, 345.
[2] Michaelis, *Annalen*, 1896, 293, 235.
[3] Jackson, Davies and Jones, *J. Chem. Soc.*, 1930, p. 2298.
[4] Michaelis, *loc. cit.*

Diethylmethylpseudocumylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_9H_{11})PI$, is isolated as white, rhombic plates, M.pt. 160° C.[1]

Diethylmethylmesitylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_9H_{11})PI$, forms colourless, glistening needles, M.pt. 125° C. with decomposition, quickly becoming brown in air.

Diethylmethylcymylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_{10}H_{13})PI$, is a non-crystalline product.

Diethylmethyl-α-naphthylphosphonium iodide, $(C_2H_5)_2(CH_3)(C_{10}H_7)PI$, crystallises from water in colourless plates, M.pt. 209° C., which are affected by sunlight, soon becoming yellow.

Di-n-propylmethylphenylphosphonium iodide, $(C_3H_7)_2(CH_3)(C_6H_5)PI$, may be recrystallised from water and melts at 137° C.[2]

Di-n-propylmethyl-p-tolylphosphonium iodide, $(C_3H_7)_2(CH_3)(C_7H_7)PI$, melts at 81·5° C. and can be crystallised from alcohol.

Di-n-butylmethylphenylphosphonium iodide, $(C_4H_9)_2(CH_3)(C_6H_5)PI$, crystallises from aqueous solution as well-defined rods, M.pt. 168° C.[3] The corresponding *ethiodide* melts at 147° C. and is best recrystallised from alcohol-ether.

Di-n-butylmethyltolylphosphonium iodide, $(C_4H_9)_2(CH_3)(C_7H_7)PI$, melts at 130·5° C.

Di-isobutylmethylphenylphosphonium iodide, $(C_4H_9)_2(CH_3)(C_6H_5)PI$, crystallises from water as pearly leaflets, M.pt. 166·5° C.[4]

Di-isobutylmethyl-p-tolylphosphonium iodide, $(C_4H_9)_2(CH_3)(C_7H_7)PI$, separates as an oil which crystallises only on long preservation.

Di-n-amylmethylphenylphosphonium iodide, $(C_5H_{11})_2(CH_3)(C_6H_5)PI$, is prepared from phenyldi-*n*-amylphosphine and methyl iodide. It forms leaflets from water, M.pt. 90·5° C.

Di-n-amylmethyl(p-ethylphenyl)phosphonium chloroplatinate, $[(CH_3)(C_8H_9)(C_5H_{11})_2P]_2PtCl_6$, forms yellow crystals of indefinite melting-point.[5]

Di-n-amylmethyl-p-tolylphosphonium iodide,[6] $(C_5H_{11})_2(CH_3)(C_7H_7)PI$, is an oil which crystallises only on long standing.

Di-isoamylmethylphenylphosphonium iodide, $(C_5H_{11})_2(CH_3)(C_6H_5)PI$, forms soft pearly flakes from water, M.pt. 181·5° C.

Di-isoamylmethyl-p-tolylphosphonium iodide, $(C_5H_{11})_2(CH_3)(C_7H_7)PI$, separates from water as hard prisms.

Di(dl-β-methylbutyl)methylphenylphosphonium iodide, $(C_5H_{11})_2(CH_3)(C_6H_5)PI$, prepared from phenyldi(*dl*-β-methylbutyl)-phosphine and methyl iodide, crystallises from water in glistening plates, M.pt. 150° C.

Di(dl-β-methylbutyl)methyl-p-tolylphosphonium iodide, $(C_5H_{11})_2(CH_3)(C_7H_7)PI$, separates from water in rods, M.pt. 131° C.

Di(δ-methylamyl)methylphenylphosphonium iodide, $(C_6H_{13})_2(CH_3)(C_6H_5)PI$, melts at 146° C., and the corresponding *ethyl compound* crystallises as glistening flakes from water, M.pt. 115·5° C.

Di(δ-methylamyl)methyl-p-tolylphosphonium iodide, $(C_6H_{13})_2(CH_3)(C_7H_7)PI$, is known, but it is difficult to crystallise.

[1] Michaelis, *Annalen*, 1897, 294, 34.
[2] Davies, Pearse and Jones, *loc. cit.*
[3] *Ibid.*
[4] *Ibid.*
[5] Jackson, Davies and Jones, *J. Chem. Soc.*, 1930, p. 2298.
[6] Davies, Pearse and Jones, *loc. cit.*

Di-n-propylmethyl-p-methoxyphenylphosphonium iodide, $(C_3H_7)_2(CH_3)(C_6H_4.OCH_3)PI$,[1] melts at 60° C.

Di-n-butylmethyl-p-methoxyphenylphosphonium chloroplatinate, $[(C_4H_9)_2(CH_3)(C_6H_4.OCH_3)P]_2PtCl_6$, forms fine yellow needles, and, after crystallisation from alcohol, melts at 196° C.

Di-n-butylmethyl-p-methoxyphenylphosphonium iodide, $(C_4H_9)_2(CH_3)(C_6H_4.OCH_3)PI$, melts at 86° C.

Di-n-amylmethyl-p-methoxyphenylphosphonium iodide, $(C_5H_{11})_2(CH_3)(C_6H_4.OCH_3)PI$, is a liquid which cannot be crystallised.

Di-n-amylmethyl-p-methoxyphenylphosphonium chloroplatinate, $[(C_5H_{11})_2(CH_3)(C_6H_4.OCH_3)P]_2PtCl_6$, separates from alcohol in yellowish-brown hexagonal plates, M.pt. 153° C.

Compounds of the Type AlkAlk'ArAr'PX.

Methylethylphenyl-p-tolylphosphonium iodide, $(CH_3)(C_2H_5)(C_6H_5)(C_7H_7)PI$, melts at 150° C., and is obtained by treating ethylphenyl-*p*-tolylphosphine with methyl iodide.[2] Treatment of the iodide with silver *d*-camphor sulphonate in dilute alcohol gives *methylethylphenyl-p-tolylphosphonium d-camphor sulphonate*, which separates from ethyl acetate as colourless needles, M.pt. 128° C. This product in dilute alcohol gives the value $[M]_D = +101{\cdot}6°$, and in absolute alcohol $[M]_D = +103{\cdot}85°$, these values giving for the phosphonium ion $[M]_D = +52{\cdot}15°$. The molecular rotation diminishes from $[M]_D = +103{\cdot}85°$ to $[M]_D = +59{\cdot}89°$ when 10 c.c. of the solution are diluted with 25 c.c. of water and filtered.

Methylethylphenylpseudocumylphosphonium iodide, $(CH_3)(C_2H_5)(C_6H_5)(C_9H_{11})PI$, is a yellow oil which yields a crystalline *platinichloride* of M.pt. 186° C.[3]

Ethylphenyl-p-tolylbenzylphosphonium iodide, $(C_2H_5)(C_6H_5)(C_7H_7)(C_6H_5.CH_2)PI$, melts at 192° C., and when converted to the *d*-camphor sulphonate gives an amorphous glassy mass which cannot be crystallised. The corresponding *bromide* deposits colourless needles from alcohol, M.pt. 215·5° C.

Methylallylphenyl-p-tolylphosphonium iodide, $(C_3H_5)(CH_3)(C_6H_5)(C_6H_4.CH_3)PI$.—22 grams of phenyl-*p*-tolylmethylphosphine, prepared from phenyl-*p*-tolylchlorophosphine and zinc dimethyl, are treated with 20 grams of allyl iodide in dry ether solution. The whole is placed in a freezing mixture and crystals soon separate. Recrystallisation from alcohol containing a little water, and finally from alcohol-ether mixture, yields colourless, glistening needles, commencing to decompose at 170° C. and melting at 175° to 177° C.[4] The iodide is soluble in water or alcohol, less soluble in acetone, insoluble in ether, benzene and light petroleum. Treatment with the silver salts of *d*-camphor-β-sulphonic acid, *d*-α-bromocamphor-π-sulphonic acid or *d*-α-bromocamphor-β-sulphonic acid only yields uncrystallisable products. Attempts to

[1] Jackson, Davies and Jones, *J. Chem. Soc.*, 1930, p. 2298.

[2] Wedekind, *Ber.*, 1912, 45, 2933; Michaelis (*Annalen*, 1901, 315, 60) gave the melting-point as 138° C.

[3] Michaelis, *loc. cit.*

[4] Pope and Gibson, *Trans. Chem. Soc.*, 1912, 101, 735; compare Radcliffe and Brindley, *Chemistry and Industry*, 1923, 42, 64.

prepare ethyl-*n*-butylphenyl-*p*-tolylphosphonium iodide and the *n*-propyl iodide from *p*-tolylphenylethylphosphine and the alkyl iodide only yield non-crystallisable oils.[1]

Methylphenyl-p-tolylbenzylphosphonium bromide, $(CH_3)(C_6H_5)(C_6H_4.CH_3)(C_6H_5.CH_2)PBr$, is the condensation product of phenyl-*p*-tolylmethylphosphine and benzyl bromide.[2] The mixture requires cooling, and the deposited crystals are recrystallised from a mixture of acetone and ether, thin, colourless plates, M.pt. 211° to 212° C., separating out. The bromide is readily soluble in acetone, insoluble in ether or benzene.

dl-Methylphenyl-p-tolylbenzylphosphonium d-α-bromocamphor - π - sulphonate, $(CH_3)(C_6H_5)(C_6H_4.CH_3)(C_6H_5.CH_2)P.O.SO_2.C_{10}H_{14}OBr$.—The foregoing bromide is treated with the corresponding amount of the silver salt of the optically active acid in hot alcohol solution, the liquid filtered and the filtrate evaporated. A gum is produced, which gradually crystallises when kept in a desiccator. Several recrystallisations from boiling benzene give colourless needles, sintering at 122° C. on rapid heating and melting at 129° to 131° C. Fractional crystallisation from ethyl acetate-acetone yields three fractions having the following specific rotations for mercury green light :

$[\alpha] = +53{\cdot}9°$, $+53{\cdot}4°$ and $+53{\cdot}9°$ in 1 per cent. aqueous solution.

The rotation constants of the salt in aqueous solution (0·2658 gram in 30 c.c. of water), examined in a 4 dm. tube at 15° C., are :

	$Mercury_{Green}$	$Mercury_{Yellow}$	$Sodium_{Yellow}$
α	+ 1·91°	+ 1·625°	+ 1·555°
$[\alpha]$	53·9°	45·85°	43·74°
$[M]$	331	282	269

The rotatory dispersions are as follows :—

$$Hg_{Green}/Na_{Yellow} = 1{\cdot}232 \qquad \text{and} \qquad Hg_{Yellow}/Na_{Yellow} = 1{\cdot}048$$

Ammonium *d*-α-bromocamphor-π-sulphonate in an aqueous solution of equivalent concentration (0·1464 gram in 30 c.c. of water) in a 4 dm. tube at 15° C., shows the following results :—

	$Mercury_{Green}$	$Mercury_{Yellow}$	$Sodium_{Yellow}$
α	+ 2·03°	+ 1·715°	+ 1·64°
$[\alpha]$	104·0°	87·9°	84·0°
$[M]$	341	288	276

[1] Radcliffe and Brindley, *loc. cit.*
[2] Pope and Gibson, *loc. cit.*

Rotatory dispersions :

$$Hg_{Green}/Na_{Yellow} = 1{\cdot}238 \qquad \text{and} \qquad Hg_{Yellow}/Na_{Yellow} = 1{\cdot}046$$

The respective fractions of the phosphonium salt, when treated in aqueous solution with potassium iodide, yield an optically inactive iodide ; hence the asymmetric phosphonium compound has not been resolved.

The *d-camphor-β-sulphonate* is prepared in a similar manner to the preceding compound. It forms colourless needles, M.pt. 134° to 137° C., readily soluble in alcohol or acetone, sparingly soluble in ethyl acetate. The following constants are obtained after fractional crystallisation from ethyl acetate-alcohol mixture, using 0·3175 gram of the salt in 30 c.c. of water in a 4 dm. tube at 15° C. :

	Hg_{Green}	Hg_{Yellow}	Na_{Yellow}
α	+ 0·52°	+ 0·42°	+ 0·39°
$[\alpha]$	12·3°	9·9°	9·2°
$[M]$	66	53	49

The rotatory dispersions are :

$$Hg_{Green}/Na_{Yellow} = 1{\cdot}333 \qquad \text{and} \qquad Hg_{Yellow}/Na_{Yellow} = 1{\cdot}075$$

The following are the values for ammonium *d*-camphor-β-sulphonate :

	Hg_{Green}	Hg_{Yellow}	Na_{Yellow}
α	+ 0·53°	+ 0·43°	+ 0·40°
$[\alpha]$	26·6°	21·6°	20·1°
$[M]$	66	54	50

The rotatory dispersions are :

$$Hg_{Green}/Na_{Yellow} = 1{\cdot}325 \qquad \text{and} \qquad Hg_{Yellow}/Na_{Yellow} = 1{\cdot}075$$

Resolution of the phosphonium salt has not been effected, since potassium iodide only yields iodides, from the various fractions, which are optically inactive.

Methylphenyl-p-tolylbenzylphosphonium iodide, $(CH_3)(C_6H_5)(C_6H_4.CH_3)(C_6H_5.CH_2)PI$, occurs when potassium iodide is added to any of the three foregoing salts in aqueous solution. It separates from alcohol in colourless, glistening plates, M.pt. 215° to 216·5° C., soluble in methyl alcohol, less soluble in hot ethyl alcohol and practically insoluble in ether, benzene or light petroleum.

Methylphenyl - p - tolylbenzylphosphonium platinichloride, $[(CH_3)(C_6H_5)(C_6H_4.CH_3)(C_6H_5.CH_2)P]_2PtCl_6$, is a yellow powder, M.pt. 214° to 215° C., formed when chloroplatinic acid is added to aqueous solutions of the foregoing salts. It is practically insoluble in the usual solvents.

Phosphonium Compounds containing Aryloxy-Groupings.[1]

Triphenoxymethylphosphonium iodide, $(C_6H_5O)_3P(CH_3)I$, occurs when triphenoxyphosphine and methyl iodide are allowed to interact. The product melts at 70° to 75° C., and is a deliquescent mass, changing to a brown oil in air, this becoming colourless on adding sodium hydroxide. The oil, when extracted with ether, dried and distilled, comes over at 190° to 195° C. at 11 mm. as a colourless liquid; this, on prolonged standing in the cold, crystallises, the melting-point being 36° to 37° C. When saponified by alcoholic potassium hydroxide and poured into fuming nitric acid the iodide yields methylphosphinic acid and dinitrophenol. This points to the saponification compound being the phenol ester of methylphosphinic acid, formed as follows :—

$$(C_6H_5O)_3P(CH_3)I + H_2O = (C_6H_5O)_2P\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ O\end{matrix} + C_6H_5OH + HI$$

Triphenoxyphosphine, when heated with *ethyl* iodide at 200° C., gives an oil which is insoluble in ether and with sodium hydroxide forms the phenol ester of ethylphosphinic acid.

Triphenoxybenzylphosphonium chloride, $(C_6H_5O)_3P(C_7H_7)Cl$, is obtained when the components are heated together at 175° C. A syrup results, which, after treating with sodium hydroxide and decomposing as above, yields the phenol ester of benzylphosphinic acid, phenol and hydrogen chloride. The *benzylphosphinic acid phenyl ester*, $C_7H_7.PO(OC_6H_5)_2$, forms small, white crystals, M.pt. 60° C., readily soluble in alcohol, ether or benzene.

Tri-p-tolyloxymethylphosphonium iodide, $(CH_3.C_6H_4O)_3P(CH_3)I$.—Tritolyloxyphosphine is obtained as an oil, B.pt. 250° to 255° C. at 10 mm.,[2] by the action of 1 molecular equivalent of phosphorus trichloride on 3 equivalents of *p*-cresol, and the phosphonium iodide is obtained from it in the usual manner. The iodide is isolated only as a syrup, which is converted by alkali to *p*-cresol, hydrogen iodide and the *p-cresyl ester* of *methylphosphinic acid*, $(CH_3.C_6H_4O)_2PO.CH_3$, a liquid, B.pt. 220° to 225° C. at 12 mm.

Tri-m-tolyloxymethylphosphonium iodide, $(CH_3.C_6H_4O)_3P(CH_3)I$.—Phosphorus trichloride and *m*-cresol yield a phosphine, B.pt. 235° to 238° C. at 7 mm. or 240° to 243° C. at 10 mm.[3] The phosphonium iodide is a colourless, crystalline, hygroscopic powder, which yields the *m-cresyl ester* of *methylphosphinic acid*, $(CH_3.C_6H_4O)_2PO.CH_3$, as a colourless liquid, B.pt. 200° to 205° C. at 7 mm.

Tripseudocumenolmethylphosphonium iodide, $[(CH_3)_3.C_6H_2O]_3P(CH_3)I$, is obtained from the pseudocumenol phosphine, which boils at 270° to 274° C. at 16 mm. In the usual way it forms the *pseudocumenol ester* of *methylphosphinic acid*, $CH_3.PO[OC_6H_2(CH_3)_3]_2$, consisting of shining crystals from ether, M.pt. 79° to 90° C.

Tri-p-chlorophenoxymethylphosphonium iodide, $(ClC_6H_4O)_3P(CH_3)I$.—The trichlorophenoxyphosphine, from phosphorus trichloride

[1] Michaelis and Kaehne, *Ber.*, 1898, 31, 1048.
[2] Compare Broeker, *J. prakt. Chem.*, 1928, [ii], 118, 287.
[3] See Broeker, *loc. cit.*

and *p*-chlorophenol at 150° C., melts at 49° C. and boils at 290° to 297° C. at 15 mm. The phosphonium iodide melts at 70° C. and may be transformed in the usual manner into the *p-chlorophenol ester* of *methylphosphinic acid*, $CH_3.PO(OC_6H_4Cl)_2$, a liquid, B.pt. about 245° C. at 20 mm.

N-*Phosphonium Compounds.*[1]

Phenyldipiperidinemethylphosphonium iodide, $C_6H_5.P(NC_5H_{10})_2.CH_3.I$.—This is produced by the interaction of phenyldipiperidine-N-phosphine and methyl iodide. It crystallises in shining tablets, M.pt. 167° C., very stable, readily soluble in alcohol, sparingly soluble in water, insoluble in ether. The corresponding *hydroxide* is a syrup; the *chloride* forms short, white needles, M.pt. 130° C., readily soluble in water, and forms a *platinichloride*, $[C_6H_5P(NC_5H_{10})_2.CH_3]_2PtCl_6$, which crystallises from hot water in yellowish-red tablets, M.pt. 178° C. The *bromide* crystallises in fine white needles. The hydroxide, when heated, splits off piperidine and yields phenylmethylphosphinic acid:

$$C_6H_5.P(NC_5H_{10})_2.CH_3.OH + H_2O = C_6H_5.P(CH_3)O.OH + 2C_5H_{10}.NH$$

Phenyldipiperidine-ethylphosphonium iodide, $C_6H_5.P(NC_5H_{10})_2.C_2H_5.I$, is prepared in a similar manner to the preceding compound. It forms slender white needles, M.pt. 174° C., and is more soluble in water than the methyl compound.

Phenyldipiperidinebenzylphosphonium chloride, $C_6H_5.P(NC_5H_{10})_2.C_7H_7.Cl$, obtained by heating together its components, forms yellowish-red plates, M.pt. 204° C.

Tri-tetrahydroquinoline-methylphosphonium iodide, $(C_9H_{10}N)_3P.CH_3.I$. —Tetrahydroquinoline combines energetically with phosphorus trichloride to yield *tri-tetrahydroquinoline-N-phosphine*, $(C_9H_{10}N)_3P$, white, rhombic plates, M.pt. 202° to 204° C. This combines with methyl iodide to give the phosphonium iodide, which crystallises in small rhombic needles, M.pt. 188° C., fairly soluble in alcohol, sparingly soluble in water and insoluble in ether. Its aqueous solution with silver oxide yields an alkaline solution of the *hydroxide*, and this with hydrochloric acid is converted to the *chloride*. Evaporation gives a solid, M.pt. 148° to 150° C., fairly soluble in alcohol and water. The *platinichloride*, $[(C_9H_{10}N)_3P.CH_3]_2PtCl_6$, forms small, glistening, reddish-yellow crystals, melting with partial decomposition at 230° C.

Phenyldi-tetrahydroquinoline-methylphosphonium iodide, $C_6H_5.P(NC_9H_{10})_2.CH_3.I$, prepared from phenyldi-tetrahydroquinoline-N-phosphine and methyl iodide, forms glistening silver voluminous needles, M.pt. 136° C.

p-Tolyldipiperidine-methylphosphonium iodide, $C_7H_7.P(NC_5H_{10})_2.CH_3.I$, obtained in the usual way, melts at 186° C. The *ethyl* derivative melts at 191° C., and the *isobutyl* and *benzyl* compounds at 204° and 125° C., respectively. All these products crystallise well, most of them in needles.

Tripiperidine-methylphosphonium hydroxide, $(C_5H_{10}N)_3P.CH_3.OH$.[2]—This compound is obtained from the corresponding iodide; it is crystalline, strongly alkaline and absorbs carbon dioxide. The

[1] Michaelis, *Ber.*, 1898, 31, 1037.
[2] Michaelis and Luxembourg, *Ber.*, 1895, 28, 2205.

bromide and *chloride* are colourless and readily soluble. The latter forms a *platinichloride*, large red crystals, M.pt. 175° C. The *iodide* is obtained from the phosphine, $(C_5H_{10}N)_3P$, isolated as a crystalline compound, M.pt. 37° to 38° C., when phosphorus trichloride interacts with piperidine in ether at 0° C.; it forms thick, colourless, cubical crystals, M.pt. 251° to 255° C. The mother liquors from the iodide deposit a substance richer in iodine, which may have the constitution $(C_5H_{10}N)_3P.3CH_3I$. The corresponding *ethylphosphonium iodide* resembles the methyl compound and melts at 178° to 179° C.; the *isobutyl compound* is a white crystalline substance, M.pt. 172° C.; the *benzylphosphonium chloride* forms a thick mass of hygroscopic crystals.

Aryl Phosphorus Betaines and Ketobetaines.

The formation of these derivatives is similar to that of the corresponding arsenibetaines. Triarylphosphines combine with monochloracetic acid to form derivatives of Type I:

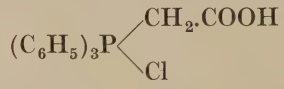
I II

These derivatives under the influence of sodium hydroxide or carbonate are transformed to the free betaines, Type II. Similar compounds may also be obtained by the oxidation by alkaline potassium permanganate of aryltrialkylphosphonium chlorides (in which the aryl group contains a substituted methyl group). If the chloracetic acid in the foregoing condensation be replaced by an aliphatic or mixed ketone, a ketonic group is introduced as in I, and the derivatives are known as ketobetaines:

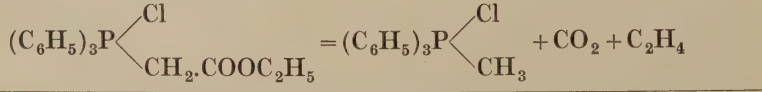
I II

Alkali transforms I to II. All the compounds are solids and yield platinichlorides.

Triphenylphosphorbetaine hydrochloride,[1]



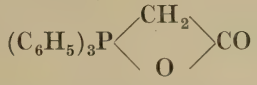
When triphenylphosphine and ethyl monochloracetate are heated together for a long time at 70° to 75° C., the *ethyl ester* of the foregoing hydrochloride results. This forms a crystalline powder, M.pt. 90° C., readily soluble in alcohol, chloroform, acetic acid or water. Its *platinichloride* crystallises from alcohol in small plates. The *betaine ester* decomposes at 172° C., but prolonged heating at 90° to 100° C. produces methyltriphenylchlorophosphine:



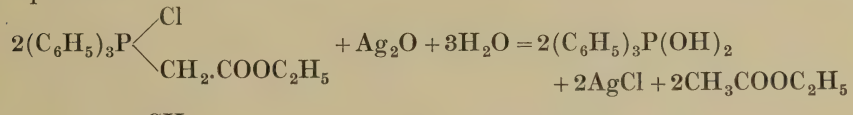
[1] Michaelis and Gimborn, *Ber.*, 1894, **27**, 272.

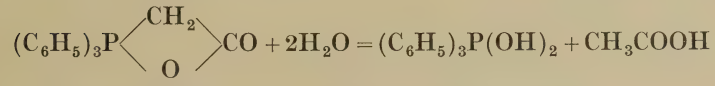
The *hydrobromide* (M.pt. 147° C.) and the *hydriodide* (M.pt. 165° to 166° C.) are isolated when the hydrochloride is treated with potassium bromide or iodide respectively.

Triphenylphosphorbetaine,

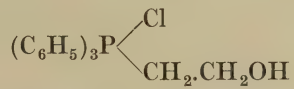


The foregoing hydrochloride when treated with silver or barium hydroxide only yields triphenylphosphine dihydroxide, $(C_6H_5)_3P(OH)_2$, but if concentrated aqueous sodium hydroxide or carbonate be used, the free betaine is isolated. It separates from alcohol in tabular crystals, M.pt. 124° to 126° C., which readily dissolve in chloroform or acetic acid, and when heated with water give the dihydroxide. It forms a *platinichloride*, consisting of long, golden-yellow needles. The decompositions mentioned above are indicated by the following equations :—



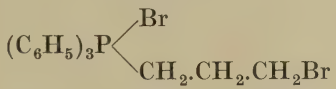


Triphenylphosphorcholine hydrochloride,



is obtained by the condensation of triphenylphosphine and ethylene chlorhydrin. It crystallises in glistening white needles, M.pt. 129° to 130° C., readily soluble in water or alcohol, insoluble in ether. Its *platinichloride* crystallises from dilute alcohol in golden-yellow needles melting with decomposition at 222° to 224° C. Moist silver oxide transforms the hydrochloride to the *free base*, a viscous liquid which is strongly alkaline and absorbs carbon dioxide from the atmosphere. The *hydrobromide* forms yellowish-white crystals, M.pt. 114° C., and the *hydriodide* melts at 185° to 186° C.

The condensation of triphenylphosphine and *trimethylene bromide* gives a *product* represented as follows :—



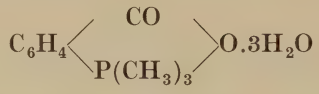
This crystallises in white needles, M.pt. 226° to 228° C., dissolving in water, but less readily in alcohol. It forms a *platinichloride* which is non-crystalline and readily decomposed.

Trimethylphosphorbenzobetaine hydrochloride,[1]

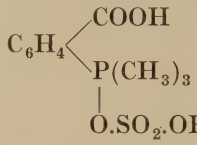
I II

[1] Michaelis and Czimatis, *Ber.*, 1882, 15, 2018.

is formed when *p*-tolyltrimethylphosphonium chloride (I) is oxidised by alkaline potassium permanganate at 55° C. It has the constitution II and forms short, thick, brilliant, transparent prisms, soluble in water or hot alcohol. The crystals have no melting-point but decompose, giving an odour of phosphine. The *platinichloride* forms a light yellow precipitate. The *free betaine*,



crystallises in rhombohedra and is efflorescent. It does not yield salts with bases, but does so with acids. The *acetate* forms fine, pearly needles ; the *nitrate* crystallises in needles ; and dilute sulphuric acid gives an *acid sulphate* which separates in needles :

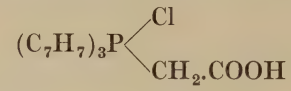


The hydrochloride decomposes as follows when heated with potassium hydroxide :

$$C_6H_4(COOH)P(CH_3)_3Cl + KOH = C_6H_5COOH + (CH_3)_3PO + KCl$$

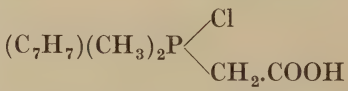
By the action of alkaline potassium permanganate on the addition product from ethylene bromide and dimethyl-*p*-tolylphosphine, a compound having the structure $C_6H_4(COOH)P(CH_3)_2O$ is obtained. This forms colourless prisms, M.pt. 243° C., having an acid taste and subliming on heating. It is very stable on heating with potassium hydroxide.

Tri-p-tolylphosphorbetaine hydrochloride,[1]



is formed in the usual manner and isolated as the *ethyl ester*, a white crystalline powder, somewhat soluble in water, and yielding tri-*p*-tolylphosphorbetaine on treatment with sodium hydroxide or carbonate. The *free betaine* separates from ether in small white crystals, M.pt. 145° C.

Dimethyl-p-tolylphosphorbetaine hydrochloride,



The *ethyl ester* of this derivative is a white, hygroscopic, crystalline powder, M.pt. 153° C., very soluble in alcohol. The *platinichloride* crystallises in fine, reddish-yellow needles, M.pt. 200° C. The hydrochloride ester is converted by sodium carbonate to the *free betaine*, a stellate mass, M.pt. 206° C. :

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[1] Michaelis and Gimborn, *loc. cit.*

$$2(CH_3)_2(C_7H_7)P(Cl)CH_2.COOC_2H_5 + Na_2CO_3 + H_2O$$
$$= 2(CH_3)_2(C_7H_7)P\begin{<}CH_2\\O\end{>}CO + 2NaCl + 2C_2H_5OH + CO_2$$

The *free hydrochloride* melts with decomposition at 172° C., and its *platinichloride* crystallises in flesh-coloured needles, M.pt. 220° C. The corresponding *diethyltolylbetaine* is hygroscopic; its *hydrochloride* melts at 96° C., and the *platinichloride* at 157° C.

α-Trimethylphosphortolubetaine hydrochloride,[1]

$$CH_3.C_6H_3\begin{<}COOH\\P(CH_3)_3Cl\end{>}$$

7 grams of 1 : 3-xylyl-4-trimethylphosphonium chloride in 1000 c.c. of water are treated with a little potassium hydroxide and the calculated amount of potassium permanganate added, the mixture being maintained at 55° C. for eight days. After filtering and evaporating to dryness, the residue is treated with alcohol, when woolly needles, insoluble in ether, are obtained. The *platinichloride* is orange-yellow and the *aurichloride* golden-yellow. The *free betaine*,

$$CH_3.C_6H_3\begin{<}CO\\P(CH_3)_3\end{>}O$$

is a hygroscopic mass. It yields a *picrate*, consisting of golden-yellow, bushy, stellate needles, M.pt. 220° C. A *nitrate*, M.pt. 226° C., a *sulphate* and an *acetate* are known. Oxidation of the hydrochloride yields *α-trimethylphosphortolubetaine hydrochloride carboxylic acid*, $(COOH)_2C_6H_3.P(CH_3)_3Cl$. This product is readily soluble in water, yields a *platinichloride*, M.pt. 258° C., and a sparingly soluble *aurichloride*. When the hydrochloride is treated with the requisite amount of silver oxide, *α-trimethylphosphortolubetaine carboxylic acid* is formed :

$$\overset{(1)}{COOH}.C_6H_3\begin{<}\overset{(3)}{CO}\\P(CH_3)_3\end{>}O$$
$$(4)$$

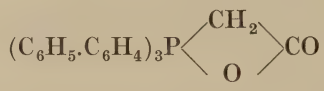
This yields glistening crystals, M.pt. 160° C., air-stable and easily soluble in water. Its *copper salt* forms blue needles, and the *silver* and *barium salts* may be crystallised from water. When the β-form of trimethylxylylphosphonium iodide is similarly oxidised, a *β-trimethylphosphortolubetaine carboxylic acid* is isolated,

$$\overset{(1)}{COOH}.C_6H_3\begin{<}\overset{(3)}{CO}\\P(CH_3)_3\end{>}O$$
$$(5)$$

[1] Conen, *Ber.*, 1898, 31, 2919.

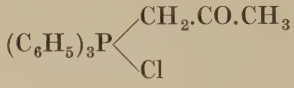
This separates from concentrated aqueous solution in fine, matted needles, M.pt. 115° C., forms a *copper salt*, consisting of blue needles, and a very hygroscopic *hydrochloride*.

Tri-biphenylphosphorbetaine,[1]

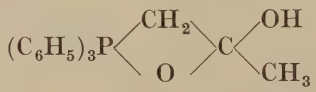


is formed by the interaction of ethyl chloroacetate and tri-biphenylphosphine at 0° C. It separates from alcohol in brilliant diamond-shaped plates, M.pt. 109° to 110° C. with preliminary softening. On standing at room temperature it is converted into tri-biphenylphosphine oxide.

Triphenylmethylphosphorketobetaine hydrochloride or **Triphenylacetonylphosphonium chloride,**[2]

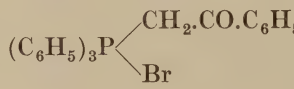


occurs when molecular proportions of triphenylphosphine and monochloracetone are heated together under reflux for forty-five minutes on the water-bath. It separates from alcohol as fine needles, melting with decomposition at 237° C., and sparingly soluble in hot benzene, insoluble in ether. The *platinichloride* is a flesh-coloured product melting with decomposition at 198° C. The *free betaine*,



is isolated by the action of sodium hydroxide or carbonate on the hydrochloride. It separates as shining needles, M.pt. 201° C., is neutral to litmus, insoluble in water, but dissolves in alcohol, benzene or ether. Treatment with the requisite acids gives the *hydrobromide*, M.pt. 226° C., and the *picrate*, citron-yellow crystals, M.pt. 166° C.

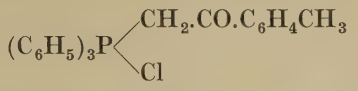
Tetraphenylphosphorketobetaine hydrobromide or **Triphenylphenacylphosphonium bromide,**



results when triphenylphosphine is condensed with bromacetophenone. It forms colourless crystals, M.pt. 273° to 274° C., soluble in alcohol or a large bulk of hot water, insoluble in ether. The *free betaine*, obtained in the usual manner, forms colourless crystals, M.pt. 183° to 184° C., soluble in alcohol or ether, insoluble in water. It forms the following salts: *hydrochloride*, fine needles, M.pt. 254° to 255° C.; *hydriodide*, pale yellow needles, melting with decomposition at 256° to 257° C.; *nitrate*, colourless needles, M.pt. 184° to 185° C., soluble in boiling water or boiling benzene.

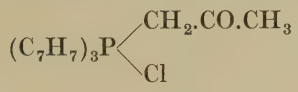
[1] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2933.
[2] Michaelis and Köhler, *Ber.*, 1899, **32**, 1566.

Triphenyl-p-tolylphosphorketobetaine hydrochloride,



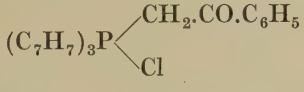
is prepared by the interaction of triphenylphosphine and chloro-*p*-tolylmethyl ketone. It crystallises in colourless needles, M.pt. 231° C., and is more soluble in water than the preceding tetraphenyl-compound. The *free betaine* forms silky needles, M.pt. 181° C., the *platinichloride*, yellowish-red needles, decomposing at 211° C., the *hydrobromide* melts at 261° C., the *hydriodide* melts at 265° C., and the *nitrate* gives slender, transparent needles, M.pt. 183° to 184° C.

Tri-p-tolylmethylphosphorketobetaine hydrochloride,



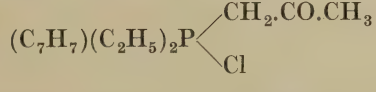
This compound is not so readily formed as the phenyl derivative and the reaction is only carried to completion when the components are heated together for five hours in a sealed tube at 80° C. The product crystallises in bushy needles, melting with decomposition at 245° C., is readily soluble in water or alcohol, sparingly soluble in benzene and insoluble in ether. The *platinichloride* melts at 220° C., and the *aurichloride* at 164° C. The *free betaine* separates from alcohol in needles, M.pt. 117° C., insoluble in water but dissolving in the usual organic solvents. It yields a *hydrobromide* melting with decomposition at 210° C., and a *hydriodide* consisting of fine needles, M.pt. 189° C.

Phenyltri-p-tolylphosphorketobetaine hydrochloride or **Tri-p-tolylphenacylphosphonium chloride,**



requires eight hours' heating in a sealed tube at 88° C. of molecular quantities of tri-*p*-tolylphosphine and monochloracetophenone to complete its preparation. It melts at 236° C., yields a *platinichloride*, M.pt. 240° C., and an *aurichloride*, M.pt. 156° C. The *free betaine* crystallises in bushy needles, M.pt. 177° C., its *hydrobromide* and *hydriodide* melting at 248° C. and 236° C. respectively.

Tolylmethyldiethylphosphorketobetaine hydrochloride,



yields a *platinichloride* consisting of reddish-yellow crystals, M.pt. 178° C., and a *picrate* forming citron-yellow needles, M.pt. 127° C., whilst the *free betaine* is a very hygroscopic solid, M.pt. 75° C.

Compounds of the Type RPX_2.

The first member of this series, namely phenyldichlorophosphine, may be isolated by passing the vapours from a mixture of benzene and

phosphorus trichloride through a red-hot porcelain tube, a slow stream of carbon dioxide being circulated through the apparatus. This method does not seem to have been applied to any other compound of this class. A more general method consists of heating together mercury diaryls and phosphorus trihalides :—

$$R_2Hg + PX_3 = RPX_2 + RHgX$$

Although this equation is given in the literature, it is very probable that the reaction takes place in stages as follows :—

$$R_2Hg + 2PX_3 = 2RPX_2 + HgX_2$$
$$R_2Hg + RPX_2 = R_2PX + RHgX$$

A higher temperature appears to facilitate the second reaction. The yields of primary product by this reaction are very poor in some cases, and the same starting materials may be used for the type R_2PX. The Friedel-Crafts reaction has also been used for these preparations :

$$C_6H_5.CH_3 + PCl_3 + [AlCl_3] = CH_3.C_6H_4.PCl_2 + HCl + [AlCl_3]$$

The resulting product is contaminated with secondary products.

All the aryldichlorophosphines are liquids which combine with the halogens forming tetrahalides, these being crystalline products decomposed by moisture into oxychlorides, $RPOCl_2$, and finally acids, $R.PO(OH)_2$. The tetrachlorides are produced also by the action of chlorinating agents, such as iodine monochloride, titanium tetrachloride or antimony pentachloride, on aryldichlorophosphines. The latter combine with oxygen to form oxychlorides, but these are best obtained by the action of sulphur dioxide or acetic acid on the tetrahalides. Similarly sulphur and aryldichlorophosphines give sulphochlorides, $RPSCl_2$, a quantitative yield occurring if the ice-cold phosphine be treated with sulphur chloride. Hydrogen sulphide reacts only to form the normal sulphide, RPS. The chlorine may be removed from phenyldichlorophosphine by silver cyanide or thiocyanate, a dicyanide or a dithiocyanate resulting. Condensation takes place between aryldichlorophosphines and aryl hydrazines, piperidine and tetrahydroquinoline, whilst the oxychlorides ($RPOCl_2$) combine with aniline, hydrazines and ammonia. The products are dealt with on pp. 86-89.

Phenyldichlorophosphine or *Phosphenyl chloride*, $C_6H_5.PCl_2$, may be prepared in several ways : (1) A mixture of benzene and phosphorus trichloride is distilled and the vapours passed through a red-hot porcelain tube.[1] The yield is greatly increased if a slow stream of carbon dioxide is passed through the apparatus during the distillation, a litre of the mixture giving 140 grams of pure product per nine hours.[2] A variation of this method consists in passing phosphorus trichloride and benzene vapours over a quartz tube sealed in a glass vessel and heated internally by a nichrome winding.[3] (2) By passing carbonyl chloride into phenylphosphine.[4] (3) When mercury diphenyl and pure

[1] Michaelis, *Annalen*, 1876, 181, 265; *Ber.*, 1873, 6, 601, 876; Köhler, *Ber.*, 1880, 13, 1623; Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 395.

[2] Pope and Gibson, *J. Chem. Soc.*, 1912, 101, 735.

[3] Bowles and James, *J. Amer. Chem. Soc.*, 1929, 51, 1406.

[4] Michaelis and Dittler, *Ber.*, 1879, 12, 338.

phosphorus trichloride are heated together in a sealed tube for several hours at 180° C., the following reaction takes place :—

$$(C_6H_5)_2Hg + PCl_3 = C_6H_5.PCl_2 + C_6H_5.HgCl$$

The yields obtained by this method are not good, 30 grams of mercury diphenyl giving only about 5 grams of pure product.[1]

The phosphine is a colourless, strongly refractive liquid, fuming in air and possessing a pungent odour resembling that of phenylphosphine. It boils at 222° C., becoming slightly brown unless distilled in an inert atmosphere ; its density is 1·319 at 20° C., and from measurements of the refractive index, the atomic refraction of phosphorus in the compound is 17·47.[2] The phosphine is soluble in benzene, chloroform or carbon disulphide, but is decomposed by water, yielding the phosphinous acid. Phosphorus readily dissolves in phenyldichlorophosphine and is difficult to remove by distillation ; in sunlight amorphous phosphorus soon separates from the solution in flocks. The phosphine combines with the halogens, oxygen and sulphur to yield tetrahalides, the oxychloride and a sulphochloride, respectively,[3] and silver cyanide and thiocyanate form a dicyanide and a dithiocyanate, respectively.[4] When the phosphine is cooled in ice and treated with sulphur chloride, a quantitative yield of the sulphochloride, $C_6H_5.PSCl_2$, results,[5] but hydrogen sulphide, if passed into the hot dichlorophosphine, gives the normal sulphide, $C_6H_5.PS$.[6] If phosphine (PH_3) be passed for several days through phenyldichlorophosphine, diphosphobenzol, $C_6H_5.P=POH$, is formed ;[7] replacement of the phosphine by phenylphosphine and slow addition of the dichlorophosphine yields phosphobenzene, $C_6H_5.P=P.C_6H_5$, if the reaction be carried out in an atmosphere of hydrogen. Warm alcohol converts the dichlorophosphine to phenylphosphinous acid,[8] and heating with mercury diphenyl in a sealed tube at 220° to 230° C. gives phenylmercuric chloride and diphenylchlorophosphine ;[9] the latter compound also results when the dichlorophosphine is heated alone for a prolonged period in a sealed tube at 280° C.[10] A solution of phosphenyl chloride (1 mol.) and phenyl hydrazine (3 mols.) in five volumes of cooled ether reacts to give phosphenyl phenylhydrazone, $C_6H_5.NH.N=P.C_6H_5$;[11] piperidine under similar conditions yields phenyldipiperidine - N - phosphine, $C_6H_5.P(NC_5H_{10})_2$,[12] whilst zinc diethyl reacts in the usual manner giving diethylphenylphosphine.[13]

Iodine monochloride, titanium chloride and antimony pentachloride react with phosphenyl chloride according to the following equations :[14]

$$C_6H_5.PCl_2 + 2ICl = C_6H_5.PCl_4 + I_2$$
$$C_6H_5.PCl_2 + 2TiCl_4 = C_6H_5.PCl_4 + Ti_2Cl_6$$
$$C_6H_5.PCl_2 + 2SbCl_5 = C_6H_5.PCl_4.SbCl_5 + SbCl_3$$

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[1] Michaelis, *loc. cit.* [2] Zecchini, *Gazzetta*, 1894, **24**, i, 34.
[3] Michaelis, *loc. cit.*; Köhler and Michaelis, *Ber.*, 1876, 9, 1053.
[4] Michaelis, *Annalen*, 1896, **293**, 212. [5] Köhler, *Ber.*, 1880, **13**, 463.
[6] Köhler and Michaelis, *Ber.*, 1877, **10**, 815.
[7] Michaelis, *Ber.*, 1875, **8**, 499; Köhler and Michaelis, *loc. cit.*
[8] Köhler and Michaelis, *loc. cit.*
[9] Michaelis and Link, *Annalen*, 1881, **207**, 193; Michaelis, *Ber.*, 1877, **10**, 627.
[10] Broglie, *Ber.*, 1877, **10**, 628.
[11] Michaelis and Oster, *Annalen*, 1892, **270**, 123.
[12] Michaelis, *Ber.*, 1898, **31**, 1037. [13] Michaelis and Ananoff, *Ber.*, 1874, 7, 1688.
[14] Köhler, *Ber.*, 1880, **13**, 1626.

The *tetrachloride*, prepared according to the preceding equations, is a crystalline compound, M.pt. 73° C., at which temperature it partly sublimes; it partially decomposes if the temperature is raised.[1] It is decomposed by water, one molecule of the latter giving the oxychloride, $C_6H_5.POCl_2$, but three molecules producing phenylphosphinic acid, $C_6H_5.PO(OH)_2$. The tetrachloride on heating at 180° C. in a sealed tube decomposes into chlorobenzene and phosphorus chloride. If sulphur dioxide or acetic acid reacts with the tetrachloride the *oxychloride* results.[2] This oxychloride [3] also occurs when oxygen combines with phosphenyl chloride, but the operation is dangerous, especially if the chloride is pure. The best method of preparation is the one using sulphur dioxide, as already mentioned. The oxychloride is a viscous liquid, B.pt. 258° C., having a faint odour, density 1·375 at 20° C. It decomposes with water according to the equation

$$C_6H_5.POCl_2 + 2H_2O = C_6H_5.PO(OH)_2 + 2HCl$$

Anilides may be formed by treating the oxychloride with amines, and twelve parts of oxychloride when heated under reflux with seven parts of phenylphosphinic acid until evolution of hydrogen chloride ceases, yield an *oxide*, $C_6H_5.PO_2$.[4] It is interesting to note that the difference between the boiling-points of phenyldichlorophosphine and the oxychloride is 36° C., whilst that between phosphorus trichloride and phosphorus oxychloride is 32° C.[5]

When one molecular proportion of bromine and a similar proportion of phenyldichlorophosphine are allowed to react, a *dibromide* is produced, $C_6H_5.PCl_2Br_2$. This product sublimes at 130° C., forming rosettes of yellowish-red, monoclinic crystals, M.pt. 208° C. Sulphur dioxide converts it into oxychloride, and when heated alone in a sealed tube at 150° C. it decomposes as follows :—

$$2C_6H_5.PCl_2Br_2 = C_6H_5.PCl_2 + PBrCl_2 + C_6H_4Br_2 + HBr$$
$$3PBrCl_2 = 2PCl_3 + PBr_3$$

A *compound*, $C_6H_5.PCl_2.Br_4$, has also been described [6] as a red mass decomposed by water into phenylphosphinous acid, hydrogen chloride, hydrogen bromide and free bromine.

Phenyldibromophosphine or *Phosphenyl bromide*, $C_6H_5.PBr_2$, may be obtained by passing dry hydrogen bromide into phosphenyl chloride, and in poor yield by the interaction of phosphorus tribromide and mercury diphenyl.[7] It is a colourless liquid, becoming yellow in sunlight and a red product separating out. Addition of bromine in ether solution gives the *tetrabromide*, consisting of stellate groups of yellowish-red needles, M.pt. 207° C., fuming in air and decomposing with a hissing sound in contact with water. A *hexabromide*, dark red needles subliming at 110° C., has also been described.

Phenyldicyanophosphine, $C_6H_5.P(CN)_2$.—When phenyldichlorophosphine reacts with silver cyanide the dicyanide is obtained as a viscous, colourless oil, B.pt. 144° to 145° C. at 20 mm., very stable

[1] Michaelis, *Annalen*, 1876, 181, 294; *Ber.*, 1873, 6, 816.
[2] Michaelis and Kammerer, *Ber.*, 1875, 8, 1306.
[3] Michaelis, *Annalen*, 1876, 181, 302; *Ber.*, 1873, 6, 816.
[4] Michaelis and Rothe, *Ber.*, 1892, 25, 1747.
[5] Michaelis, *Ber.*, 1873, 6, 816.
[6] Michaelis, *Annalen*, 1876, 181, 294.
[7] Michaelis and Köhler, *Ber.*, 1876, 9, 519.

towards water. It is readily decomposed by dilute alkali to the metal cyanide and phosphinic acid.[1]

Phenyldithiocyanophosphine, $C_6H_5.P(SCN)_2$, is a viscous yellow oil, B.pt. 205° to 207° C. at 20 mm. It is sparingly soluble in cold water and is energetically decomposed when the solution is heated. A violent reaction takes place with chlorine with formation of the tetrachloride, $C_6H_5.PCl_4$, sulphur and cyanogen chloride.[2]

Phenylphosphorus sulphide, $C_6H_5.PS$,[3] occurs when hydrogen sulphide is passed into phenyldichlorophosphine or when the hydrosulphide, $C_6H_5.PSH_2$ (a pale yellow liquid obtained from phenylphosphine and sulphur), is heated for a prolonged period. It has a vile odour and is an oily product yielding diphenylphosphinic acid when oxidised by nitric acid. In the first method of preparation a second sulphide, $(C_6H_5)_4P_2S_3$, is formed. This is a white crystalline solid, M.pt. 190° to 193° C., unaffected by water but yielding diphenylphosphinic acid when treated with nitric acid.

Phenyldichlorosulphophosphine, $C_6H_5PSCl_2$.—Phenyldichlorophosphine dissolves sulphur forming the sulphochloride, but the latter is obtained in quantitative yield by the interaction of phenyldichlorophosphine and sulphur chloride.[4] It fumes feebly in air, and prolonged boiling with water gives phenylphosphinic acid, hydrogen chloride and hydrogen sulphide. The reaction with potassium hydroxide is violent, and if the solution be evaporated to dryness and the residue taken up in alcohol, needles separate; these have the composition, $C_6H_5.PS(OK)_2$, and when the alcohol solution is diluted with water, the free *acid*, $C_6H_5.PS(OH)_2$, is obtained. A very dilute alcohol solution of lead acetate gives lead sulphide when boiled with a similar solution of the sulphochloride. The sulphochloride is soluble in alcohol, water precipitating an oil, $C_6H_5.PS(OC_2H_5)_2$, and phenol giving $C_6H_5.PS(OC_6H_5)_2$.

p-Chlorophenyldichlorophosphine, $ClC_6H_4.PCl_2$.[5]—From a mixture containing 150 grams of chlorobenzene, 200 grams of phosphorus trichloride and 30 parts of anhydrous aluminium chloride, a 25 per cent. yield of the phosphine, calculated on the weight of chlorobenzene used, is obtained. It boils at 253° to 255° C., has density 1·425 at 17° C., and fumes slightly in air. The position of the chlorine atoms is determined by heating the product in a sealed tube for two hours at 150° C. with bromine, when the phosphorus is replaced by bromine. The corresponding *tetrachloride* is a crystalline, deliquescent compound, and the *chlorobromide* a fuming solid, M.pt. 216° C. The *oxychloride*, prepared from the tetrachloride by the action of sulphur dioxide, is a faintly yellow liquid, B.pt. 284° to 285° C., density 1·4892 at 20° C.

p-Bromophenyldichlorophosphine, $BrC_6H_4.PCl_2$, is a viscous, refractive liquid, B.pt. 271° to 272° C., density 1·6895 at 15° C.[6] Heated with bromine and water in a sealed tube it gives *p*-dibromobenzene. The *tetrachloride* is a yellow mass, M.pt. 55° C., and the *oxychloride* a liquid, B.pt. 290° to 291° C.

[1] Michaelis, *loc. cit.*
[2] Michaelis, *Annalen*, 1896, **293**, 213.
[3] Michaelis and Köhler, *loc. cit.*
[4] Köhler and Michaelis, *Ber.*, 1876, **9**, 1053; Köhler, *Ber.*, 1880, **13**, 463.
[5] Michaelis, *Annalen*, 1896, **293**, 223; Maecker, *Inaug. Dissert. Rostock*, 1893.
[6] Michaelis, *loc. cit.*; Gundermann, *Inaug. Dissert. Rostock*, 1894.

o-Tolyldichlorophosphine, $CH_3.C_6H_4.PCl_2$, occurs when mercury di-*o*-tolyl is heated with ten to fifteen times its weight of phosphorus trichloride in a sealed tube at 180° to 190° C. for forty-eight hours. The yield is 78 per cent.[1] It is a colourless, highly refractive liquid, B.pt. 244° C., density 1·3067 at 18·5° C. The *tetrachloride* forms a yellowish-white, crystalline mass, M.pt. 63° to 66° C., and the *oxychloride* is a colourless liquid, B.pt. 273° C., density 1·3877 at 18·5° C.

o-Chlorotolyldichlorophosphine, $(CH_3)ClC_6H_3.PCl_2$, is a transparent, highly refractive liquid, B.pt. 265° to 266° C., density 1·373 at 22° C. The corresponding *tetrachloride* crystallises from benzene as pale yellow needles, and with sulphur dioxide yields the *oxychloride*, M.pt. 36° C., B.pt. 290° to 291° C.[2]

m-Tolyldichlorophosphine, $CH_3.C_6H_4.PCl_2$, obtained from mercury di-*m*-tolyl and phosphorus trichloride, boils at 235° C. and has a density of 1·282 at 22° C. The *tetrachloride* is a viscous yellow oil, solidifying at about 0° C., and the *oxychloride* is a transparent liquid, B.pt. 275° C., density 1·3533 at 18° C.[3]

p-Tolyldichlorophosphine, $CH_3.C_6H_4.PCl_2$, may be obtained from mercury di-*p*-tolyl and phosphorus trichloride or directly from toluene by the action of phosphorus trichloride in the presence of aluminium chloride.[4] It crystallises in needles or leaflets, M.pt. 25° C., B.pt. 245° C. The *tetrachloride* forms small columns from benzene, M.pt. 42° C., deliquescing in the air and forming the *oxychloride*. The latter is also isolated by treating the tetrachloride with sulphur dioxide; it forms a viscous oil, B.pt. 284° to 285° C., water converting it into the phosphinic acid. More recent work on the tetrachloride [5] gives the melting-point as 69° to 91° C., and shows that when heated at 98° C. in a current of dry air it evolves hydrogen chloride, whilst chlorination of the methyl group occurs. The *chlorobromide*, $C_7H_7.PCl_2Br_2$, melts at 128° to 130° C. in a sealed tube with elimination of bromine. Reduction of the dibromide with sulphur dioxide gives the substance $CH_3.C_6H_4.POClBr(?)$, M.pt. 5° to 8° C.

p-Tolyldibromophosphine gives a *tetrabromide*, $C_7H_7.PBr_4$, M.pt. 160° to 161° C. with elimination of bromine; hydrogen bromide is evolved when the compound is kept at 160° C.

Cymyldichlorophosphine, $(C_3H_7)CH_3.C_6H_3.PCl_2$,[6] occurs when 15 grams of cymene, 20 grams of phosphorus trichloride and 3 grams of aluminium chloride are heated together for twenty hours. The yield is about 2 grams. The product is a transparent, highly refractive liquid, B.pt. 275° to 278° C., possessing a characteristic odour. It readily reacts with chlorine and bromine, the *tetrachloride* being a viscous, non-crystallisable liquid.

p-Anisyldichlorophosphine, $CH_3O.C_6H_4.PCl_2$, is a colourless, strongly refractive liquid, B.pt. 150° C. at 18 mm. or 245° to 253° C.

[1] Michaelis and Paneck, *Annalen*, 1882, **212**, 213; Michaelis, *Annalen*, 1896, **293**, 292; Schmidt, *Inaug. Dissert. Rostock*, 1895.

[2] Melchiker, *Ber.*, 1898, **31**, 2915; *Chem. Zentr.*, 1899, i, 129.

[3] Michaelis, *Annalen*, 1896, **293**, 302; Berghegger, *Inaug. Dissert. Rostock*, 1894.

[4] Michaelis and Lange, *Ber.*, 1875, **8**, 1313; Michaelis, *Ber.*, 1879, **12**, 1009; Michaelis and Paneck, *Ber.*, 1880, **13**, 653; *Annalen*, 1882, **12**, 206; Michaelis, *Annalen*, 1896, **293**, 261; Wedekind, *Ber.*, 1912, **45**, 2933; Radcliffe and Brindley, *Chemistry and Industry*, 1923, **42**, 64.

[5] Lindner, *Monatsh.*, 1923, **53** and **54**, 263.

[6] Michaelis, *Annalen*, 1897, **294**, 54.

at 760 mm., density 1·331 at 25° C.[1] The *tetrachloride*[2] yields colourless, stellate groups of needles, M.pt. 35° to 40° C., deliquescent in air, forming the *oxychloride*, a yellowish liquid boiling above 360° C. with partial decomposition, but boiling unchanged at about 173° C. at 12 to 15 mm.[3]

p-Phenetyldichlorophosphine, $C_2H_5O.C_6H_4.PCl_2$, forms a colourless, unpleasant, fuming liquid, boiling at 266° C. with slight decomposition.

p-Ethylphenyldichlorophosphine, $C_2H_5.C_6H_4.PCl_2$, boils at 250° to 252° C., and has a density of 1·227 at 17° C. The *tetrachloride* forms white crystals, M.pt. 51° C., and the *oxychloride* is a colourless liquid, B.pt. 294° C., density 1·29 at 16° C.[4]

o-Xylyldichlorophosphine, $(CH_3)_2C_6H_3.PCl_2$, boils at 278° C., and the corresponding *oxychloride* melts at 145° C.[5]

m-Xylyldichlorophosphine, $(CH_3)_2C_6H_3.PCl_2$, is a faintly fuming, strongly refractive liquid, the boiling-point being given as 256° to 258° C. when prepared from mercury di-*m*-xylyl, and 265° C. when prepared from *m*-xylene. Its density is 1·24 at 18° C.[6]

p-Xylyldichlorophosphine, $(CH_3)_2C_6H_3.PCl_2$, boils at 253° to 254° C. and crystallises at −30° C. to colourless needles, density 1·25 at 18° C. The *tetrachloride* is a pale yellow crystalline mass, M.pt. 60° C., and the *oxychloride* a viscous liquid, B.pt. 280° to 281° C., density 1·31 at 18° C.[7]

Pseudocumyldichlorophosphine, $(CH_3)_3C_6H_2.PCl_2$, is isolated as a colourless liquid, B.pt. 280° C., density 1·2356 at 20° C.; the *tetrachloride* is a pale green crystalline mass, M.pt. 75° C.; the *oxychloride* melts at 63° C. and boils at 307° to 308° C.[8]

Mesityldichlorophosphine, $(CH_3)_3C_6H_2.PCl_2$, crystallises in transparent plates, M.pt. 35° to 37° C., B.pt. 273° to 275° C., density 1·205 at 15° C.; the *tetrachloride* is a yellowish crystalline mass, M.pt. 70° C., and the *oxychloride* forms large transparent tablets, M.pt. 92° to 93° C., B.pt. above 360° C.[9]

Cumyldichlorophosphine, $(CH_3)_2CH.C_6H_4.PCl_2$, is a colourless liquid, B.pt. 268° to 270° C., density 1·190 at 12° C. The *tetrachloride* forms a white crystalline mass, M.pt. 53° to 55° C., and the *oxychloride* boils at 183° C. at 35 mm. or 295° to 300° C. at 760 mm. with decomposition.[10]

Diphenylmethanedichlorophosphine, $C_6H_5.CH_2.C_6H_4.PCl_2$.—This compound is prepared by the interaction of 40 grams of diphenylmethane, 65 grams of phosphorus trichloride and 5 grams of aluminium chloride, the yield being 10 to 15 per cent. on the weight of hydrocarbon used. It is a colourless, viscous liquid, B.pt. 221° C. at 20 mm., density 1·182 at 17° C., yielding a yellow, crystalline *tetrachloride*,

[1] Jackson, Davies and Jones, *J. Chem. Soc.*, 1930, p. 2298.
[2] Michaelis, *loc. cit.*
[3] Michaelis, *Annalen*, 1896, **293**, 248.
[4] Michaelis, *Annalen*, 1896, **293**, 315; Lewschinski, *Inaug. Dissert. Rostock*, 1893.
[5] Michaelis and Paneck, *Annalen*, 1882, **212**, 237; Michaelis, *loc. cit.*; Weller, *Inaug. Dissert. Rostock*, 1888.
[6] Weller, *Ber.*, 1887, **20**, 1718.
[7] Weller, *Ber.*, 1888, **21**, 1492.
[8] Michaelis, *Annalen*, 1897, **294**, 2; Rothe, *Inaug. Dissert. Rostock*, 1892.
[9] Michaelis, *loc. cit.*; Hecker, *Inaug. Dissert. Rostock*, 1893.
[10] Michaelis, *loc. cit.*; Meyer, *Inaug. Dissert. Rostock*, 1893; Uster, *Inaug. Dissert. Rostock*, 1896.

M.pt. 80° C., and an *oxychloride*, B.pt. 261° C. at 20 mm., density 1·207.[1]

Dibenzyldichlorophosphine, $C_6H_5.CH_2.CH_2.C_6H_4.PCl_2$, is a pale yellow liquid, B.pt. 250° C. at 60 mm., crystallising on cooling to 2° C. The *tetrachloride* melts at 65° C., and the *oxychloride* at 75° C.

Diphenyldichlorophosphine, $C_6H_5.C_6H_4.PCl_2$, is a viscous liquid which slowly crystallises at 0° C. and melts at 5° C. Its density is 1·3098 at 14° C.

α-Naphthyldichlorophosphine,[2] $C_{10}H_7.PCl_2$, is obtained from mercury di-α-naphthyl :

$$2PCl_3 + (C_{10}H_7)_2Hg = HgCl_2 + 2C_{10}H_7.PCl_2$$
$$2C_{10}H_7.PCl_2 + (C_{10}H_7)_2Hg = HgCl_2 + 2(C_{10}H_7)_2PCl$$

It should be noted that arsenic and antimony trichlorides behave in a similar manner. A more recent method of preparation uses the Friedel-Crafts reaction, when naphthalene and phosphorus trichloride give a 15 per cent. yield of α-naphthyldichlorophosphine.[3] Chlorination yields a *tetrachloride*, and bromine forms a *dibromide* melting at 114° to 116° C. Hydrolysis of the tetrachloride gives α-naphthylphosphinic acid.

Condensation Products obtained from Compounds of the Types $RPCl_2$, $RPCl_4$ *and* $RPOCl_2$.

Phenylphosphenphenylhydrazone, $C_6H_5.P : N.NH.C_6H_5$.[4]— Phenyldichlorophosphine (1 mol.) and phenylhydrazine (3 mols.) are allowed to react in five volumes of cooled ether, the reaction being complete when a test portion of the filtered liquid is free from chlorine, this stage being reached in about thirty minutes. The product is filtered, the residue washed with ether and the filtrate allowed to stand for several hours, when fine needles separate. The reaction is as follows :—

$$C_6H_5.PCl_2 + 3C_6H_5.NH.NH_2 = C_6H_5.P : N.NH.C_6H_5 + 2C_6H_5.NH.NH_2.HCl$$

The product crystallises from ethyl acetate as small, hard plates, M.pt. 152° C., easily soluble in chloroform, less soluble in alcohol or ether. It reduces Fehling's solution on heating, is stable towards alkali, but with acids yields phenylhydrazine and phenylphosphinous acid ; when boiled for a long period with water a complex of the two latter compounds separates.

When the starting materials in the foregoing preparation are brought together in ether and the phenylhydrazine hydrochloride filtered off, the addition of water to the dry mass gives a white powder. This may be crystallised from chloroform, and is the *dihydrazide*, $C_6H_5.P(NH.NH.C_6H_5)_2$.

Phenylphosphentolylhydrazone, $C_6H_5.P : N.NH.C_6H_4.CH_3$, is formed when tolylhydrazine is used in the foregoing preparation. It forms small, colourless prisms, M.pt. 162° C., and it is split into its components when boiled with water.

[1] Michaelis, *Annalen*, 1901, 315, 43; Güsewell, *Inaug. Dissert. Rostock*, 1895.
[2] Kelbe, *Ber.*, 1878, 11, 1499.
[3] Lindner and Strecker, *Monatsh.*, 1929, 53 and 54, 274.
[4] Michaelis and Oster, *Annalen*, 1892, 270, 129.

Phenylphosphenbenzylhydrazone, $C_6H_5.P : N.NH.CH_2.C_6H_5$, crystallises in colourless needles, M.pt. 141° C., and resembles the preceding compounds in its properties.

Chlorophenylphosphenphenylhydrazone, $ClC_6H_4.P : N.NH.C_6H_5$, yields white, silky plates, melting with decomposition at 161° C.[1]

Mesitylphosphenphenylhydrazone, $C_9H_{11}.P : N.NH.C_6H_5$, forms small, silky needles, M.pt. 135° C.

Phenyldipiperidine-N-phosphine,[2] $C_6H_5.P(NC_5H_{10})_2$, occurs when phenyldichlorophosphine reacts with piperidine in ether solution, the operation being completed by warming the mixture for two hours on the water-bath. The product separates as white plates, M.pt. 78° C., having a faint odour of piperidine. It readily dissolves in ether, benzene or alcohol, but is insoluble in water. It combines with carbon disulphide forming two compounds, (*a*) $C_6H_5.P(NC_5H_{10})_2.2CS_2$, a yellowish-white powder, M.pt. 144° C., and (*b*) $C_6H_5.P(NC_5H_{10})_2.CS_2$, yellow needles, M.pt. 137° C.; the latter may be extracted from the former by repeated crystallisation from benzene and ether. When the phosphine is treated with dry chlorine gas in ether solution, a *dichloride* is produced, which is deliquescent in air and is decomposed by water with the formation of an *oxide*, $C_6H_5.PO(NC_5H_{10})_2$. The latter is best obtained, however, by treating the oxychloride ($C_6H_5.POCl_2$) with piperidine (4 mols.) in ether solution; it is a white, crystalline, hygroscopic mass, M.pt. 68° C., soluble in alcohol or ether, insoluble in water or dilute hydrochloric acid, but decomposed by concentrated hydrochloric acid.

Phenylditetrahydroquinoline-N-phosphine, $C_6H_5.P(NC_9H_{10})_2$, obtained from phenyldichlorophosphine and tetrahydroquinoline, forms warty crystals, M.pt. 150° C., readily soluble in benzene, sparingly soluble in ether or alcohol. It is stable towards water, but decomposed by dilute acid. The *oxide*, $C_6H_5.PO(NC_9H_{10})_2$, crystallises as short, white needles, M.pt. 216° C., and is very stable.

Phenylphosphinic diamide, $C_6H_5.PO(NH_2)_2$.[3]—This compound is produced when the oxychloride ($C_6H_5.POCl_2$) is treated with concentrated ammonium hydroxide. It separates from alcohol as white, glistening scales, M.pt. 189° C., and when boiled with water yields the ammonium salt of phenylphosphinic acid.

Phenylphosphinic dianilide, $C_6H_5.PO(NH.C_6H_5)_2$, results when the ammonium hydroxide in the preceding preparation is replaced by aniline. It forms white needles, M.pt. 211° C.

Phenylphosphinic anilide, $C_6H_5.PO(NH.C_6H_5)OH$, occurs when aniline hydrochloride is used in the foregoing preparation. It is a white, crystalline powder, M.pt. 125° C., and its *chloride* is formed as a by-product in the reaction. The *phenyl ester*, $C_6H_5.PO(NH.C_6H_5)OC_6H_5$, is obtained by the action of pure phenol on a mixture of the chloride and the anilide; it forms small, yellowish-white crystals, M.pt. 83° C., B.pt. 235° C. at 25 mm., from which aniline is eliminated on boiling with concentrated alkali.

Phenylphosphinic phenylhydrazide, $C_6H_5.PO(NH.NH.C_6H_5)_2$, is isolated when four molecular equivalents of phenylhydrazine react with one molecular equivalent of the oxychloride ($C_6H_5.POCl_2$). It

[1] Michaelis, *Annalen*, 1896, **293**, 236.
[2] Michaelis, *Ber.*, 1898, **31**, 1037.
[3] Michaelis, *Annalen*, 1896, **293**, 213.

crystallises in white, silky needles, M.pt. 175° C., stable towards alkali but decomposed by acids.

p-Tolylphosphinic diamide, $CH_3.C_6H_4.PO(NH_2)_2$, crystallises as white, glistening plates, M.pt. 176° C. The *dianilide* forms small, pearly needles, M.pt. 209° C. The latter, when treated with bromine, yields mono- and dibromo-anilines and *p*-tolylphosphinic acid, and with alkaline potassium permanganate *p*-carboxyphenylphosphinic acid is formed.

p-Tolylphosphinic anilide, $CH_3.C_6H_4.PO(NH.C_6H_5)OH$, is obtained in a similar manner to the corresponding phenyl compound. It melts at 150° C., and shows decomposition when crystallised from alcohol or acetic acid. The *copper salt* is a light blue powder, and the *phenyl ester* a viscous, highly refractive oil, B.pt. 283° C. at 48 mm., solidifying after long standing to a crystalline mass, M.pt. 59° C.

p-Tolylphosphinic di-p-toluidide, $CH_3.C_6H_4.PO(NH.C_6H_4.CH_3)_2$, forms snow-white glistening needles, M.pt. 237° C.; the corresponding *acid*, $CH_3.C_6H_4.PO(NH.C_6H_4.CH_3)OH$, is a white powder, M.pt. 208° C., the *phenyl ester* of which melts at 48° C. and boils at 280° C. at 32 mm.

p-Tolylphosphinic diphenylhydrazide, $CH_3.C_6H_4.PO(NH.NH.C_6H_5)_2$, crystallises as fine, matted needles, M.pt. 171° C., readily decomposed by acids, but not so easily by alkalis.

p-Tolyldipiperidine-N-phosphine, $CH_3.C_6H_4.P(NC_5H_{10})_2$, obtained in a similar manner to the corresponding phenyl compound, crystallises from ether as large, monoclinic crystals, M.pt. 80° C.[1] With *carbon disulphide* it gives an *addition product*, $C_7H_7.P(NC_5H_{10})_2.2CS_2$, pale yellow crystals, M.pt. 139° C.

p-Tolylditetrahydroquinoline - N - phosphine, $CH_3.C_6H_4.P(NC_9H_{10})_2$, forms white needles, M.pt. 140° C., sparingly soluble in ether, alcohol or benzene. The corresponding *oxide* gives long, white needles, M.pt. 181° C.

p-Carboxyphenylphosphinic amide, $NH_2.CO.C_6H_4.PO(OH)_2$.[2] —When *p*-carboxyphenylphosphinic acid (1 part) is treated with 3 parts of phosphorus pentachloride, an acid chloride is produced, $ClCO.C_6H_4.POCl_2$. The latter in benzene solution, treated with ammonium carbonate or dry ammonia, gives the required amide. The amide is best isolated in the form of its *silver salt*. Treatment of the foregoing acid chloride with aniline gives *p-carboxyphenylphosphinic anilide*, $C_6H_5.NH.CO.C_6H_4.PO(NH.C_6H_5)_2$, a white, crystalline product, M.pt. 242° C., only slowly affected by boiling acid or alkali.

Pseudocumylphosphinic dianilide, $C_9H_{11}.PO(NH.C_6H_5)_2$, forms small, white, silky needles, M.pt. 197° C., very stable towards hot dilute acids and alkali. The oxychloride, $C_9H_{11}.POCl_2$, when heated with aniline salts in xylene solution, yields a *phosphazo-derivative*, $C_9H_{11}.PO : N.C_6H_5$.

Pseudocumylphosphinic diphenylhydrazide, $C_9H_{11}.PO(NH.NH.C_6H_5)_2$, separates as white, glistening needles, M.pt. 208° C., and reduces Fehling's solution on warming.

Phenyltrianilidophosphonium chloride, $(C_6H_5.NH)_3C_6H_5.PCl$,[3] is formed when the tetrachloride, $C_6H_5.PCl_4$, is heated for a long time

[1] Michaelis, *Ber.*, 1898, 31, 1046.
[2] Michaelis, *Annalen*, 1896, 293, 280.
[3] Michaelis and Kuhlmann, *Ber.*, 1895, 28, 2212.

with aniline hydrochloride at about 200° C. It gives blue-tinted needles, M.pt. 250° C. The corresponding *bromide* melts at 235° C., the *iodide* at 165° C., the *nitrate* at 160° C., and the *hydroxide* at 216° C.

Chlorophenyldichlorophosphine and *piperidine* condense to form a *product* of M.pt. 95° C. The corresponding *anisyldichloro-derivative* melts at 69° C. and the *phenetyl compound* at 84° C. These form phosphonium iodides and combine with carbon disulphide.[1]

p-Tolyltrianilidophosphonium chloride, $(C_6H_5.NH)_3C_7H_7.PCl$, forms colourless, slender needles, M.pt. 245° C., and the *platinichloride* crystallises in golden-yellow plates. Sodium hydroxide converts the chloride into the *hydroxide*, a colourless glistening powder, M.pt. 240° C., from which a *nitrate*, M.pt. 180° C., a *bromide*, M.pt. 238° C., and an *iodide*, M.pt. 235° C., have been obtained.

Pseudocumyltrianilidophosphonium chloride, $(C_6H_5.NH)_3C_9H_{11}.PCl$, is a white, crystalline powder, M.pt. 247° C., from which the following derivatives may be isolated : *bromide*, a white crystalline powder, M.pt. 259° C. ; *iodide*, M.pt. 220° C. ; *nitrate*, M.pt. 224° to 225° C. ; *hydroxide*, stellate groups of needles, M.pt. 203·5° C., indifferent to litmus.

p-Tolylphosphinic phenyl ester, $CH_3.C_6H_4.PO(OC_6H_5)_2$,[2] is obtained from one molecular proportion of the oxychloride, $C_7H_7.POCl_2$, and two molecular proportions of phenol at 120° to 130° C. It is a viscous liquid having a bluish fluorescence and boiling above 360° C. Water decomposes it into phenol and *p*-tolylphosphinic acid. When only one proportion of phenol is used in the preparation, an *ester chloride* results, $CH_3.C_6H_4.POCl(OC_6H_5)$; this is a white, crystalline mass, M.pt. 55° C., B.pt. above 360° C. The free acid is unknown, but a *silver salt* has been isolated, together with the following derivatives : an *amide*, $CH_3.C_6H_4.PO(NH_2)(OC_6H_5)$, M.pt. 115° to 116° C. ; a *phenylhydrazide*, $CH_3.C_6H_4.PO(OC_6H_5)(NH.NH.C_6H_5)$, small white needles, M.pt. 173° to 174° C. ; a *piperidide*, $CH_3.C_6H_4.PO(OC_6H_5)(NC_5H_{10})$, a viscous yellow oil ; a *p-cresyl ester*, $CH_3.C_6H_4.PO(OC_7H_7)_2$, a viscous liquid, B.pt. above 360° C., yielding an *ester chloride*, M.pt. 60° C. ; a *pyrocatechol ester*, M.pt. 81° C., B.pt. above 360° C., its *ester chloride* being a thick, colourless liquid, B.pt. above 360° C.

Pseudocumylphosphinic diphenyl ester,[3] $C_9H_{11}.PO(OC_6H_5)_2$, is produced either by the action of sodium phenolate on the oxychloride ($C_9H_{11}.POCl_2$) or from phenol and the tetrachloride ($C_9H_{11}.PCl_4$). It is a viscous, colourless liquid, B.pt. above 360° C., density 1·172 at 15° C. After standing for some months it becomes solid, M.pt. 62·5° C., and is stable to dilute alkali but saponified by alcoholic alkali.

Compounds of the Types R_2PX and $RR'PX$.

These types of phosphines may be obtained by the interaction of aryldichlorophosphines and mercury diaryls or arylmercuric halides :

$$RPCl_2 + R_2Hg = R_2PCl + RHgCl$$
$$RPCl_2 + RHgCl = R_2PCl + HgCl_2$$

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[1] Michaelis, *Ber.*, 1898, 31, 1037; Rocher, *Inaug. Dissert. Rostock*, 1896.
[2] Michaelis, *Annalen*, 1896, 293, 213.
[3] Michaelis, *ibid.*, 1897, 294, 8.

In the case of dipseudocumylchlorophosphine, it occurs during the preparation of the primary phosphine. All the compounds are high-boiling, viscous liquids, which may be oxidised to the corresponding phosphinic acids, $R_2PO(OH)$. Treatment with chlorine converts them into trichlorides, R_2PCl_3, which are readily decomposed by water yielding phosphinic acids. In several cases oxychlorides are known.

A number of interesting condensation products may be isolated from diarylchlorophosphines, of which the following is an example: Diphenylchlorophosphine and sodium ethoxide react to form ethyl diphenylphosphinite, $(C_6H_5)_2P.OC_2H_5$, the by-product in this reaction being ethyl diphenylphosphinate, $(C_6H_5)_2PO.OC_2H_5$. Under the catalytic influence of ethyl iodide at the ordinary temperature the phosphinite is transformed to ethyldiphenylphosphine oxide, $(C_2H_5)(C_6H_5)_2PO$. If the sodium ethoxide be replaced by sodium mercaptide, ethyl diphenylthiophosphinite results, $(C_6H_5)_2P.SC_2H_5$, the by-product being ethyl diphenyloxythiophosphinate, $(C_6H_5)_2PO.SC_2H_5$. In some cases under the catalytic action of alkyl iodides the thiophosphinites are transformed to sulphides, *e.g. iso*propyl diphenylthiophosphinite gives *iso*propyldiphenylphosphine sulphide, $(C_3H_7)(C_6H_5)_2PS$.

Diphenylchlorophosphine, $(C_6H_5)_2PCl$.—Mercury diphenyl, 35 grams, and 30 grams of phosphenyl chloride are heated together at 220° to 230° C., the mass extracted with benzene and filtered. The solvent is removed and the residue fractionated, the pure product distilling at 320° C. and having a density of 1·2293 at 15° C. It is a viscous oil, only slightly attacked by water, but exposure to the air or boiling with concentrated nitric acid oxidises it to diphenylphosphinic acid. Treatment with chlorine gives a *trichloride*, $(C_6H_5)_2PCl_3$, readily decomposed by water.[1]

Di-p-tolylchlorophosphine, $(CH_3.C_6H_4)_2PCl$, is a colourless oil, B.pt. 345° to 350° C., yielding a pale yellow *trichloride* and an *oxychloride* in the form of a viscous oil boiling above 360° C.

Di-p-tolylthiochlorophosphine, $(CH_3.C_6H_4)_2PSCl$.[2] — Toluene (200 to 250 grams), 200 grams of phosphorus sulphochloride and 30 grams of aluminium chloride are heated together in an oil-bath, first at 126° to 130° C., then at 180° C. until the evolution of hydrogen chloride ceases. The dark brown liquid is shaken with petroleum ether and after twelve hours the solvent is distilled off, the residue heated to 126° C. to remove phosphorus sulphochloride, then shaken many times with petroleum ether. The pale yellow solution is poured off from the black residue and yellow crystals separate. Crystallisation from acetic acid gives white needles, M.pt. 96° C. The mother-liquors contain primary and secondary *p*-tolylthiochlorophosphines.

Dipseudocumylchlorophosphine, $[(CH_3)_3C_6H_2]_2PCl$,[3] is formed together with the primary phosphine when aluminium chloride is used as a catalyst in the interaction of phosphorus trichloride and *pseudo*cumene, but the product is difficult to isolate in a pure state. The boiling-point is 305° C., and chlorine reacts with the crude product yielding a mixture of *trichlorides*, which when treated with water give a *monobasic acid*, M.pt. 212° C., and a *dibasic acid*, M.pt. 203° C.

[1] Michaelis, *Ber.*, 1877, 10, 627; Michaelis and Link, *Annalen*, 1881, 207, 193.
[2] Michaelis, *Annalen*, 1901, 315, 64.
[3] Michaelis, *loc. cit.*

Phenyl-p-tolylchlorophosphine, $(C_6H_5)(C_7H_7)PCl$,[1] may be prepared as follows: (1) Phenyldichlorophosphine, 78 grams, and 60 grams of *p*-tolylmercuric bromide are heated together in a flask at 270° C. for two to three hours. A reflux condenser is then attached to the flask and through this a stream of carbon dioxide is circulated. The reaction is very vigorous at first; after its completion the mass is cooled, extracted with benzene, the extract filtered and fractionally distilled. The product boils at 230° to 240° C. at 100 mm., the yield being 30 grams, or 63·5 per cent. (2) *p*-Tolyldichlorophosphine, 30 grams, and 35 grams of mercury diphenyl are heated together for two hours at 270° C., and after cooling, the mass is treated with dry benzene, the extract filtered and fractionated in a carbon dioxide atmosphere. Phenyl-*p*-tolylchlorophosphine is a vile-smelling, colourless liquid, which yields a bright yellow crystalline *trichloride* when treated with chlorine.

Phenylpseudocumylchlorophosphine, $(C_6H_5)(C_9H_{11})PCl$, occurs[2] in 25 to 30 per cent. yield when 40 grams of mercury diphenyl and 30 grams of *pseudo*cumyldichlorophosphine react together. The product boils normally at 356° C. or at 208° C. at 10 mm. The *trichloride* crystallises in light yellow flakes, and the *oxychloride* is a liquid, B.pt. 210° to 215° C. at 10 mm.

Diphenylbenzylphosphine dichloride,[3] $(C_6H_5)_2(C_7H_7)PCl_2$, is formed when diphenylchlorophosphine is heated at 180° C. with an excess of benzyl chloride. It melts at 187° C., is insoluble in ether and benzene, and is quickly decomposed by alcohol or water to *diphenylbenzylphosphine oxide*, $(C_6H_5)_2(C_7H_7)PO$, consisting of small white prisms, M.pt. 195° to 196° C. It is interesting to note that under similar conditions triphenylphosphine dichloride forms the dihydroxide. Nitration of the oxide by mixed acid yields *trinitrodiphenylbenzylphosphine oxide*, $(C_6H_4.NO_2)_2(C_7H_6.NO_2)PO$, colourless crystals from acetic acid, M.pt. 206° C., reduced by tin and hydrochloric acid.

Condensation Products from Compounds of the Type R_2PX.

Ethyl diphenylphosphinite, $(C_6H_5)_2P.OC_2H_5$,[4] is formed when diphenylchlorophosphine in ether solution is treated with sodium ethoxide. The product is a transparent liquid, B.pt. 179° C. at 14 mm., density 1·0896 at 0° C. It forms an *additive compound* with *copper iodide*, M.pt. 190° to 191° C. Under the catalytic influence of ethyl iodide at ordinary temperature it is transformed into ethyldiphenylphosphine oxide. During the preparation of the phosphinite some *ethyl diphenylphosphinate*, $(C_6H_5)_2PO(OC_2H_5)$, is obtained as a by-product.

Ethyl diphenylthiophosphinite, $(C_6H_5)_2P.SC_2H_5$,[5] is the condensation product of diphenylchlorophosphine and sodium ethyl mercaptide. It is a liquid, B.pt. 196·5° to 197° C. at 13 mm., density 1·1330. It gives *double salts* with *copper halides*. The by-product in

[1] Michaelis, *Annalen*, 1901, **315**, 59; Söchtig, *Inaug. Dissert. Rostock*, 1894; Wedekind, *Ber.*, 1912, **45**, 2933; Pope and Gibson, *Trans. Chem. Soc.*, 1912, **101**, 735; Radcliffe and Brindley, *Chemistry and Industry*, 1923, **42**, 64.

[2] Michaelis, *Ber.*, 1877, **10**, 627; Michaelis and Link, *loc. cit.*

[3] Dörken, *Ber.*, 1888, **21**, 1505.

[4] Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 395.

[5] Arbusoff, *ibid.*, p. 549.

this preparation is *ethyl diphenyloxythiophosphinate*, $(C_6H_5)_2PO.SC_2H_5$, M.pt. 72° to 73° C.

isoPropyl diphenylphosphinite, $(C_6H_5)_2P.OC_3H_7$, boils at 160° C. at 8 mm., has a density of 1·0925 at 0° C., and forms a crystalline *additive compound* with *copper iodide*, M.pt. 114° to 115° C. *isoPropyl diphenylphosphinate*, $(C_6H_5)_2PO.OC_3H_7$, M.pt. 95° to 96° C., is formed as a by-product.

isoPropyl diphenylthiophosphinite, $(C_6H_5)_2P.SC_3H_7$, occurs only in small quantity when diphenylchlorophosphine reacts with sodium *iso*propyl mercaptide. It boils at 229° to 230° C. at 28 mm., and rapidly isomerises under the influence of *iso*propyl iodide to *iso*propyldiphenylphosphine sulphide.

isoButyl diphenylphosphinite, $(C_6H_5)_2P.OC_4H_9$, boils at 202° to 203° C. at 11 mm., has a density of 1·0311 at 17° C., and forms a crystalline *additive compound* with *copper iodide*. In its preparation *iso*butyl diphenylphosphinate, $(C_6H_5)_2PO.OC_4H_9$, M.pt. 77° C., is the by-product, together with a little diphenylphosphinic acid.

isoButyl diphenylthiophosphinite, $(C_6H_5)_2P.SC_4H_9$, from sodium *iso*butyl mercaptide and diphenylchlorophosphine, is a colourless liquid, B.pt. 200·5° to 201° C. at 8 mm., density 1·0892 at 0° C., forming an *additive compound* with *copper iodide*. Under the catalytic influence of *iso*butyl iodide at 115° C. it yields *iso*butyldiphenylphosphine sulphide.

isoAmyl diphenylthiophosphinite, $(C_6H_5)_2P.SC_5H_{11}$, is a liquid, B.pt. 219° to 220° C. at 12 mm., density 1·0645 at 17° C.

Ethyl phenylethylphosphinate, $(C_6H_5)(C_2H_5)PO.OC_2H_5$, is formed by the isomerisation of diethyl phenylphosphinite under the catalytic influence of ethyl iodide. It boils at 162° to 164° C. at 16 mm., and on hydrolysis forms *ethylphenylphosphinic acid*, M.pt. 79° to 80° C.

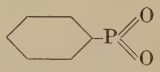
Compounds of the Type RPO_2.

This type of oxide has no parallel in the arsenical compounds. The compounds are prepared by heating dried arylphosphinic acids with the corresponding oxychlorides :

$$C_6H_5.PO(OH)_2 + C_6H_5.POCl_2 = 2C_6H_5.PO_2 + 2HCl$$

They may also be obtained by dehydrating arylphosphinic acids by means of phosphorus pentachloride, but the resulting products are not so crystalline as those obtained by the former method. All the compounds are crystalline solids, water converting them into the corresponding acids.

Phenylphosphinoxide,[1]



Seven grams of phenylphosphinic acid are dried and heated with 12 grams of the corresponding oxychloride, $C_6H_5.POCl_2$, in a reflux apparatus until the evolution of hydrogen chloride ceases, when the product is washed with cold benzene and then taken up in warm benzene. The solution is first frozen, then carefully thawed, and the solvent

[1] Köhler and Michaelis, *Ber.*, 1877, 10, 807; Michaelis and Rothe, *Ber.*, 1892, 25, 1747.

poured off, the residue being dried at 70° C. in a stream of carbon dioxide. The resulting product is a white, crystalline powder, M.pt. 100° C., readily soluble in benzene. Exposure to moist air converts it into phenylphosphinic acid. If the latter acid be dehydrated by means of phosphorus pentachloride, the oxide produced is not so crystalline as that isolated by the previous method.

Chlorophenylphosphinoxide, $ClC_6H_4.PO_2$, is readily formed when the dry phosphinic acid is heated with the oxychloride in dry benzene for two hours. It is a white, glistening, crystalline powder, M.pt. 211° C., soluble in hot benzene and readily transformed to the acid by water.

Bromophenylphosphinoxide, $BrC_6H_4.PO_2$, is a white powder, M.pt. 185° to 186° C., only sparingly soluble in benzene.

p-Tolylphosphinoxide, $CH_3.C_6H_4.PO_2$, has similar properties to the phenyl compound and melts at 101° C. The corresponding *o-tolyl-compound* crystallises in compact prisms, but no melting-point is recorded.

p-Anisylphosphinoxide, $CH_3O.C_6H_4.PO_2$, is a white powder, M.pt. 52° C., readily soluble in benzene but insoluble in petroleum ether; it fumes in the air and is easily converted into the acid.[1]

Pseudocumylphosphinoxide, $C_9H_{11}.PO_2$, crystallises from benzene in small leaflets or prisms, M.pt. 216° C., and is less readily attacked by water than the phenyl and tolyl compounds.[2]

Mesitylphosphinoxide, $C_9H_{11}.PO_2$, forms very small crystals melting with decomposition at 215° to 216° C.

Diphenylmethanephosphinoxide, $C_{13}H_{11}.PO_2$, prepared from the acid and oxychloride in the usual manner, is a snow-white powder, M.pt. 169° C., soluble in hot benzene or chloroform. Water slowly converts it into the phosphinic acid.[3]

Triarylphosphine Oxides and Sulphides.

Unlike the tertiary arsines, the tertiary phosphines do not yield stable dihalides of the type R_3PX_2,[4] these being obtained only as syrups which yield dihydroxides on treatment with alkalis. Dehydration of the dihydroxides over sulphuric acid gives the oxides, R_3PO. Nitration of the triaryldihydroxides by mixed acid yields trinitrotriarylphosphine oxides, which may be reduced to amino-oxides in the usual way. Solution of triarylphosphines in fuming nitric acid forms dinitrates, $R_3P(NO_3)_2$, which may be transformed into hydroxynitrates by prolonged standing over lime and concentrated sulphuric acid. Compounds containing the benzyl radical are obtained by special methods.

The triarylphosphine oxides are solids, and those which do not contain nitro- or amino-groups substituted in the benzene ring yield double salts with many metal chlorides, such derivatives having well-defined crystalline forms.

Triarylphosphines in carbon disulphide or ether solution dissolve sulphur to give crystalline sulphides.

[1] Michaelis, *Annalen*, 1896, 293, 254.
[2] Michaelis and Rothe, *loc. cit.*; Michaelis, *Annalen*, 1897, 294, 8.
[3] Michaelis, *Annalen*, 1901, 315, 45.
[4] A possible exception is tri*pseudo*cumylphosphine, which forms a relatively stable dibromide.

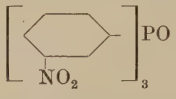
Triphenylphosphine dihydroxide, $(C_6H_5)_3P(OH)_2$.—If bromine be added to triphenylphosphine, a thick syrup is obtained which decomposes on the addition of sodium hydroxide with formation of the dihydroxide:[1]

$$(C_6H_5)_3PBr_2 + 2NaOH = (C_6H_5)_3P(OH)_2 + 2NaBr$$

The bromine may be replaced by chlorine or the phosphine in concentrated hydrochloric acid can be treated with potassium chlorate. The dihydroxide crystallises from benzene-petroleum ether solution in long, thin, white prisms, M.pt. 148° C., insoluble in water, soluble in alcohol.

Triphenylphosphine oxide, $(C_6H_5)_3PO$, results when the dihydroxide is dried over sulphuric acid or heated to 100° C. with water. It melts at 153·5° C. and boils above 360° C. without decomposition. It forms the following double salts:[2] *Triphenylphosphine oxide hydrogen ferrocyanide,* $2(C_6H_5)_3PO.H_4Fe(CN)_6$, small, colourless needles, turning green on exposure to light, insoluble in water; *triphenylphosphine oxide hydrogen cobalticyanide,* $(C_6H_5)_3PO.H_3Co(CN)_6.3H_2O$, transparent, indefinite, prismatic crystals, M.pt. 172° C.; *triphenylphosphine oxide hydrogen aurichloride,* $2(C_6H_5)_3PO.AuCl_4$, flat, yellow, hexagonal plates, M.pt. 179° C.; *triphenylphosphine oxide trichloracetate,* $(C_6H_5)_3PO.CCl_3COOH$, colourless, rhombic crystals, M.pt. 97° to 99° C.; *triphenylphosphine oxide hydrogen chloride,* $(C_6H_5)_3PO.HCl$, white, cubic crystals, M.pt. 185° C.; *triphenylphosphine oxide cadmium iodide,* $2(C_6H_5)_3PO.CdI_2$, stout, white prisms, M.pt. 192·5° C.; *triphenylphosphine oxide zinc chloride* and *zinc iodide,* general formula $2(C_6H_5)_3PO.ZnX_2$, the *chloride* crystallising as small colourless prisms, the *iodide* as small, colourless rhombs, M.pt. 223° to 226° C.; *triphenylphosphine oxide cobalt chloride,* $2(C_6H_5)_3PO.CoCl_2$, deep blue, cubic crystals, M.pt. 233° C.

Tri-m-nitrotriphenylphosphine oxide,[3]



5 grams of triphenylphosphine dihydroxide are added to a mixture of 10 grams of nitric acid and 25 grams of concentrated sulphuric acid maintained at 15° to 20° C. The clear solution is poured into cold water, the precipitate removed, washed with water and boiled with alcohol, a heavy crystalline powder resulting. Purification is effected by boiling with acetic acid and adding four volumes of alcohol to the cooled solution, faint yellow needles separating, which become white on repeated recrystallisation. The yield is 85 to 90 per cent. The compound melts at 243° C., explodes at higher temperatures, dissolves readily in hot acetic acid, but is insoluble in the usual solvents.

Tri-m-aminotriphenylphosphine oxide, $(C_6H_4.NH_2)_3PO$.—To a mixture of 30 parts of tin and 100 to 150 parts of concentrated hydrochloric acid, 10 parts of the preceding nitro-derivative are slowly added and the mixture warmed until the tin dissolves and the nitro-

[1] Michaelis and Gleichmann, *Ber.*, 1882, **15**, 801; Michaelis and Soden, *Annalen*, 1885, **229**, 295; *Ber.*, 1884, **17**, 921.

[2] Pickard and Kenyon, *Trans. Chem. Soc.*, 1906, **89**, 262.

[3] Michaelis and Soden, *Ber.*, 1884, **17**, 921.

compound disappears. The reaction mixture is then diluted with water, treated with hydrogen sulphide to remove the tin, and after filtration an excess of sodium hydroxide added to the filtrate. The white precipitate is washed with water and crystallised from boiling alcohol, snow-white prisms, M.pt. 259° C., being obtained; these are soluble in hot water or acetone, and form salts with acids, these salts dissolving in water. Neutral solutions of the salts yield yellow precipitates with platinic chloride. The *acetyl derivative* melts at 187·5° C., and the *benzoyl derivative* at 180° C. The base with bromine water gives a white precipitate having the composition $[C_6H_2Br_2(NH_2)]_3PO$, M.pt. 205° to 206° C., and methylation of the base by methyl iodide in a sealed tube at 100° C. gives the base $[C_6H_4.N(CH_3)_2]_2PO(C_6H_4.NH_2)$, white needles, M.pt. 182° to 186° C.

Triphenylphosphine dinitrate, $(C_6H_5)_3P(NO_3)_2$.—Triphenylphosphine dissolves in fuming nitric acid with evolution of heat, and the mixture, when poured into water, yields a yellow oil which gradually solidifies and crystallises. The product appears to be a mixture of the dinitrate and dihydroxide and changes completely into the latter on standing in air. Evaporation of the fuming nitric acid solution on the water-bath gives the nitrate as a yellow crystalline mass. After standing for eight days over lime and concentrated sulphuric acid, the nitrate is transformed into the *hydroxynitrate*, $(C_6H_5)_3P(OH)NO_3$, M.pt. 75° C. Nitration of the phenyl group cannot be effected by fuming nitric acid alone, but takes place when a mixture of nitric and sulphuric acids is used.

Triphenylphosphine sulphide, $(C_6H_5)_3PS$.[1]—Triphenylphosphine in carbon disulphide solution combines directly with sulphur to yield the sulphide, and thiocyanic acid or thiocyanogen also gives some sulphide when it reacts with the phosphine.[2] The sulphide crystallises from alcohol in long, brilliant needles, M.pt. 150° to 151° C., readily soluble in alcohol, benzene, chloroform or carbon disulphide, insoluble in water or ether.

Triphenylphosphine sulphide and diphenylketene in molecular proportions react to form triphenylphosphine oxide and thioketene.[3]

Triphenylphosphine selenide,[4] $(C_6H_5)_3PSe$, melts at 183° to 184° C.

Tri-p-tolylphosphine oxide, $(CH_3.C_6H_4)_3PO$, crystallises from benzene-ligroin as small needles, M.pt. 145° C.; the *sulphide* and *selenide* both crystallise in needles, melting at 182° C. and 189° C. respectively.

Chlorophenyldi-p-tolylphosphine oxide, $(ClC_6H_4)(CH_3.C_6H_4)_2PO$, separates as long, bushy needles, M.pt. 130° C., the corresponding *selenide* as short, white needles, M.pt. 172° C., and the *sulphide* as small, white crystals, M.pt. 149° C. Oxidation of the oxide by chromic oxide and acetic acid gives the *dicarboxy-acid*, $(ClC_6H_4)(COOH.C_6H_4)_2PO.OH$, as white plates.

p-Tolyldipiperidine-N-phosphine oxide,[5] $(CH_3.C_6H_4)(NC_5H_{10})_2PO$, crystallises in white, hygroscopic needles, M.pt. 60° C., and the corresponding *sulphide* is very stable, melting at 88° C.

[1] Michaelis and Gleichmann, *Ber.*, 1882, 15, 801.
[2] Challenger, Smith and Paton, *Trans. Chem. Soc.*, 1923, 123, 1046.
[3] Staudinger, Rathsam and Kjilsberg, *Helv. Chim. Acta*, 1920, 3, 853.
[4] Michaelis and Soden, *loc. cit.*
[5] Michaelis, *Ber.*, 1898, 31, 1037.

Tribenzylphosphine oxide, $(C_6H_5.CH_2)_3PO$.—Benzal chloride at 130° C. is treated with phosphonium iodide in small quantities, when a violent reaction ensues ; the whole operation is conducted in a carbon dioxide atmosphere. A resinous mass results and this is decomposed by heating with water or alcohol.[1] The reaction is represented by the following equations :—

$$C_6H_5.CHCl_2 + 2PH_4I = C_6H_5.CH_2Cl + 2PH_3 + I_2 + HCl$$
$$3C_6H_5.CH_2Cl + PH_3 + I_2 = (C_6H_5.CH_2)_3PI_2 + 3HCl$$
$$(C_6H_5.CH_2)_3PI_2 + H_2O = (C_6H_5.CH_2)_3PO + 2HI$$

The oxide also occurs as a by-product when phosphonium iodide and benzaldehyde are digested together for four to five hours at 100° C.,[2] the following equation indicating the course of the reaction :—

$$2PH_4I + 4C_6H_5.CHO = C_6H_5.CH_2.PO(OH)_2 + (C_6H_5.CH_2)_3PO + 2HI$$

The oxide crystallises from alcohol as white, transparent needles, M.pt. 213° C., soluble in benzene, ether and chloroform, and subliming without decomposition.[3] It is very stable and is unacted upon by reducing agents such as hydrogen iodide or sulphur dioxide. Its alcohol solution yields double salts with metal chlorides, the following being known : With *palladium chloride*, $[(C_7H_7)_3PO]_3.PdCl_2$, a brownish-red mass ; with *ferric chloride*, $[(C_7H_7)_3PO]_3.2FeCl_3$, light yellow prisms ; with *mercuric chloride*, $[(C_7H_7)_3PO]_3.HgCl_2$, colourless prisms or pyramids ; with *cobalt chloride*, $[(C_7H_7)_3PO]_3.CoCl_2$, blue needles ; with *platinic chloride*, $[(C_7H_7)_3PO]_4.H_2PtCl_6$, yellow needles,[4] M.pt. 240° to 241° C. ; also with *hydrogen chloride*, $(C_7H_7)_3PO.HCl$, M.pt. 169° C., is formed with gas evolution, solidifying and remelting at 208° to 210° C. ; with *chloroauric acid*, $[(C_7H_7)_3PO]_2.HAuCl_4$, flat, yellow, hexagonal plates, M.pt. 222·5° C. ; with *magnesium methyl iodide*, $[(C_7H_7)_3PO]_2.CH_3MgI$, small, colourless needles or prisms, M.pt. 163° to 166° C.

Tri-p-nitrotribenzylphosphine oxide, $(C_7H_6.NO_2)_3PO$,[5] is formed by nitration of the foregoing oxide with nitric acid (density 1·5) at 0° C. It separates from dilute acetic acid as colourless needles, M.pt. 273° C., sparingly soluble in chloroform, acetone, benzene or alcohol, insoluble in light petroleum. Oxidation with 2 per cent. alkaline permanganate solution gives *p*-nitrobenzoic acid.

Tri-biphenylphosphine oxide,[6] $(C_6H_5.C_6H_4)_3PO$, is prepared by treating the phosphine with bromine in ether, and heating the oily dibromide obtained in the presence of air. It also occurs when tri-biphenylbenzylphosphonium bromide reacts with alcoholic potash. It crystallises from alcohol containing a little ammonia in flat, needle-like crystals, M.pt. 233° to 234° C.

Tri-m-xylylphosphine oxide, $(C_8H_9)_3PO$, has been described, but no melting-point is given. The corresponding *sulphide* forms prisms, M.pt. 167° C.

[1] Fleissner, *Ber.*, 1880, **13**, 1665.
[2] Litthauer, *Ber.*, 1889, **22**, 2144.
[3] Fleissner, *loc. cit.*
[4] Pickard and Kenyon, *Trans. Chem. Soc.*, 1906, **89**, 262; compare Fleissner, *loc. cit.*; Letts and Collie, *Trans. Roy. Soc. Edin.*, 1888, **30**, pt. i, 181.
[5] Challenger and Peters, *J. Chem. Soc.*, 1929, p. 2610; compare Collie, *Trans. Chem. Soc.*, 1889, **55**, 223.
[6] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2933.

Tri-p-xylylphosphine oxide, $(C_8H_9)_3PO$, melts at 173° C., and the corresponding *sulphide* at 170° C.

Tripseudocumylphosphine oxide, $(C_9H_{11})_3PO$, yields prisms, M.pt. 222° C., and the *sulphide* melts at 192° C.

Mixed Phosphine Oxides and Sulphides.

Two types of mixed phosphine oxides are known, namely, $AlkAr_2PO$ and Alk_2ArPO. The former may be obtained by the action of heat on alkyltriarylphosphonium hydroxides, *e.g.*

$$(C_6H_5)_3P(CH_3)OH = (C_6H_5)_2(CH_3)PO + C_6H_6$$

or by treating diarylchlorophosphines with sodium alkoxides. Another important method of producing these oxides is based on the fact that alkyl diarylphosphinites under the catalytic influence of alkyl iodides undergo isomerisation to alkyldiarylphosphine oxides :

$$Ar_2P.OAlk \longrightarrow Alk.Ar_2PO$$

The oxides Alk_2ArPO are obtained by oxidation of the corresponding phosphines or heating the phosphonium hydroxides.

Dialkylarylphosphines in carbon disulphide or ether solution dissolve sulphur with the formation of sulphides, which are crystalline solids. Alkyldiarylphosphine sulphides are obtained in a similar manner to the corresponding oxides by isomerisation of thiophosphinites, $R_2P.SR'$, under the catalytic influence of alkyl iodides :

$$Ar_2P.SAlk \longrightarrow AlkAr_2PS$$

Methyldiphenylphosphine oxide, $(CH_3)(C_6H_5)_2PO$, may be isolated by the reactions indicated in the following equations :—[1]

$$2(C_6H_5)_3P(CH_3)I + Ag_2O + H_2O = 2(C_6H_5)_3P(CH_3)OH + 2AgI$$
$$(C_6H_5)_3P(CH_3)OH = (C_6H_5)_2CH_3.PO + C_6H_6$$

An aqueous solution of methyltriphenylphosphonium iodide or chloride is treated with freshly precipitated silver oxide and boiled with water until a filtered test portion of the solution shows no turbidity with silver nitrate. The mixture is then entirely filtered and the filtrate evaporated to dryness on the water-bath. The residue is extracted with ether, the solvent removed and the product crystallised from ether, prisms resulting, M.pt. 110° to 111° C. The oxide has also been prepared by the interaction of diphenylchlorophosphine and sodium methoxide,[2] when it melts at 109° to 110° C., methyldiphenylphosphine occurring as a by-product. When obtained by heating an alcohol solution of methyltribiphenylphosphonium iodide with moist silver oxide, it crystallises in needles, M.pt. 223° to 224° C.[3]

Ethyldiphenylphosphine oxide, $(C_2H_5)(C_6H_5)_2PO$, occurs when the phosphonium compound is treated with silver oxide as before, or can be obtained from ethyl diphenylphosphinite, $(C_6H_5)_2P.OC_2H_5$, under the catalytic influence of ethyl iodide at room temperature. It separates from boiling ether in colourless, glistening prisms, M.pt. 121° C.

[1] Michaelis and Soden, *Annalen*, 1885, **229**, 295.
[2] Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 395.
[3] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2933.

isoPropyldiphenylphosphine oxide, $(C_3H_7)(C_6H_5)_2PO$,[1] crystallises in prisms, M.pt. 145° to 146° C., and is formed quantitatively by heating *iso*propyl diphenylphosphinite with *iso*propyl iodide at 115° C.

isoButyldiphenylphosphine oxide, $(C_4H_9)(C_6H_5)_2PO$.—*iso*Butyl diphenylphosphinite, when heated at 120° C. with *iso*butyl iodide, is isomerised to the oxide, which forms needles, M.pt. 137·5° to 138° C.

isoAmyldiphenylphosphine oxide, $(C_5H_{11})(C_6H_5)_2PO$,[2] separates from boiling water as small, stellate groups of needles, M.pt. 96° to 97° C.

Dimethyl-p-tolylphosphine oxide, $(CH_3)_2(CH_3.C_6H_4)PO$.[3]—The phosphine is suspended in a large bulk of water and treated with the calculated quantity of mercuric oxide, the latter soon becoming reduced and the odour of phosphine apparent. After filtering and evaporating, a yellow oil remains, which crystallises to a stellate, hygroscopic mass, M.pt. 95° C. This oxide is not attacked by fuming nitric acid, but a mixture of one part of concentrated nitric acid and two parts of concentrated sulphuric acid causes nitration to occur; the nitrated product is diluted with water, partially neutralised with sodium hydroxide, the neutralisation being completed by sodium carbonate; evaporation to dryness and extraction of the residue with alcohol then yields an oil which deposits yellow prisms, M.pt. 175° C., when dried over sulphuric acid. This *nitro-compound* is soluble in water, alcohol or acetic acid, but insoluble in ether, benzene and carbon disulphide; it yields a *mercurichloride*, consisting of white needles, M.pt. 127° C.

Dimethyl-p-carboxyphenylphosphine oxide, $(CH_3)_2(COOH.C_6H_4)PO$, occurs when the foregoing oxide is oxidised by alkaline potassium permanganate in the usual manner. It forms colourless crystals, M.pt. 240° C., B.pt. above 360° C. at 15 mm., readily soluble in water, alcohol or acetic acid, insoluble in ether or benzene. The corresponding *mercurichloride* separates from hot water as white needles, M.pt. 154° C.; the *aurichloride* yields shining, colourless, rhombic plates; the *platinichloride* crystallises as hard, rhombic plates, M.pt. 234° C.; the *ammonium salt* is deposited from alcohol-ether as needles, melting with decomposition at 212° C.; the *silver salt* forms small, hard crystals, and the *copper salt* is a blue-green powder. Equimolecular proportions of the oxide and phosphorus pentachloride give an *acid chloride*, $(CH_3)_2(ClCO.C_6H_4)PO$, not obtained pure enough for analysis, but yielding an *anilide*, $(CH_3)_2(C_6H_5.NH.CO.C_6H_4)PO$, which separates from 30 per cent. alcohol in pearly plates, M.pt. 235° C.

Diethylphenylphosphine oxide, $(C_2H_5)_2(C_6H_5)PO$,[4] melts at 55° to 56° C., B.pt. above 360° C. It deliquesces on exposure to the air.

Diethyl-p-tolylphosphine oxide, $(C_2H_5)_2(CH_3.C_6H_4)PO$,[5] melts at 74° C., and yields a mercurichloride, M.pt. 135° C.

Diphenylbenzylphosphine oxide, $(C_6H_5)_2(C_6H_5.CH_2)PO$,[6] obtained from diphenylchlorophosphine and sodium benzyloxide, melts at 192° to 193° C.

Diethylbenzylphosphine oxide, $(C_2H_5)_2(C_6H_5.CH_2)PO$, occurs

[1] Arbusoff, *loc. cit.*
[2] Michaelis and Soden, *loc. cit.*
[3] Michaelis, *Annalen*, 1896, **293**, 283; Miething, *Inaug. Dissert. Rostock*, 1895.
[4] Michaelis and Ananoff, *Ber.*, 1874, **7**, 1688; Michaelis, *loc. cit.*
[5] Michaelis, *loc. cit.*, p. 235.
[6] Arbusoff, *loc. cit.*

when diethylbenzylphosphine is oxidised by exposure to the air or treatment with nitric acid. The product is much purer if obtained by heating the phosphonium hydroxide :

$$(C_2H_5)_2(C_6H_5.CH_2)_2P.OH = (C_2H_5)_2(C_6H_5.CH_2)PO + C_7H_8$$

The oxide boils at 328° to 330° C. and crystallises in long needles, which react with sodium giving the free phosphine. It thus differs from trimethylphosphine and triethylphosphine, which are unaffected by sodium.

Allyldi-biphenylphosphine oxide,[1] $(C_3H_5)(C_6H_5.C_6H_4)_2PO$, occurs when allyltribiphenylphosphonium bromide is treated with hot alcoholic potash. It forms microscopic crystals, softening above 160° C. and melting to a cloudy liquid at 192° to 193° C. The product contains one molecule of alcohol of crystallisation.

Diethylbenzylphosphine sulphide,[2] $(C_2H_5)_2(C_6H_5.CH_2)PS$, occurs when sulphur is added to an ether solution of the phosphine. It melts at 94° to 95° C. and boils with partial decomposition at 300° to 310° C. When heated with metallic sodium, a violent reaction takes place and free phosphine is produced.

The *thiophosphinites* of the type $R_3P.SR'$ under the catalytic influence of alkyl iodides undergo isomerisation into the sulphides $R_2R'.PS$, the process being similar to that occurring with the corresponding oxygen compounds, but in the case of the sulphides complicated by the formation of by-products.[3]

Ethyldiphenylphosphine sulphide, $(C_2H_5)(C_6H_5)_2PS$, occurs when ethyl diphenylthiophosphinite, $(C_6H_5)_2P.SC_2H_5$, is heated with ethyl iodide in a sealed tube at 100° C. It crystallises in rhombic tablets, M.pt. 65·5° to 66° C.

isoPropyldiphenylphosphine sulphide, $(C_3H_7)(C_6H_5)_2PS$, is rapidly produced when *iso*propyl iodide and *iso*propyl diphenylthiophosphinite are heated together at 99° C., the product crystallising in thin tablets, M.pt. 97° to 98° C.

isoButyldiphenylphosphine sulphide, $(C_4H_9)(C_6H_5)_2PS$, is obtained in quantitative yield when *iso*butyl diphenylthiophosphinite is heated with *iso*butyl iodide at 115° C., but prolonged heating of the mixture at 80° C. gives di-*iso*butyldiphenylphosphonium iodide. The sulphide separates as rhombic crystals, M.pt. 80° to 81° C.

isoAmyldiphenylphosphine sulphide, $(C_5H_{11})(C_6H_5)_2PS$.—The isomerisation in this case takes place at 120° C., the sulphide crystallising as large, bright, rhomboidal crystals, M.pt. 63·5° C.

Phenyldipiperidine-N-phosphine sulphide,[4] $C_6H_5.P(NC_5H_{10})_2S$, occurs when sulphur is heated with the phosphine at 130° C. It crystallises as white needles, M.pt. 92° C., which are very stable.

Tri-biphenylphosphine sulphide,[5] $(C_6H_5.C_6H_4)_3PS$, obtained from the interaction of the phosphine and carbon disulphide saturated with sulphur, forms microscopic plates, M.pt. 241° to 242° C., with preliminary softening.

[1] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2933.
[2] Collie, *Trans. Chem. Soc.*, 1888, **53**, 714, 720.
[3] Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 549.
[4] Michaelis, *Ber.*, 1898, **31**, 1037.
[5] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2933.

Acids of the Types $RP(OH)_2$, $RPO(OH)_2$ and $R_2PO.OH$.

The phenyl derivatives of these acids were known in 1873, that is, two years before the corresponding arsenical compounds, the method of preparation of the phosphorus derivatives subsequently being applied to obtain the arsenical acids. In the latter case the development of the diazo-reaction as a means of obtaining the desired product ousted the older methods, but this reaction does not seem to have met with success in the case of the phosphorus acids. The principal methods for preparing the acids are shown by the following equations :—

$$R.PCl_2 + 2H_2O = RP(OH)_2 + 2HCl$$
$$R.PCl_2 + 2C_2H_5OH = RP(OH)_2 + 2C_2H_5Cl$$
$$R.PCl_4 + 3H_2O = RPO(OH)_2 + 4HCl$$
$$R.POCl_2 + 2H_2O = RPO(OH)_2 + 2HCl$$
$$R_2.PCl_3 + 2H_2O = R_2PO.OH + 3HCl$$

The acids of the type $RP(OH)_2$ are all solids, readily forming metal salts and double salts with arylhydrazines. No nitro- or amino-acids are known, and those containing halogen in the ring are not obtained by direct halogenation, but by using halogenated phosphines as starting materials. The esters are formed by treating aryldichlorophosphines with sodium alkoxides.

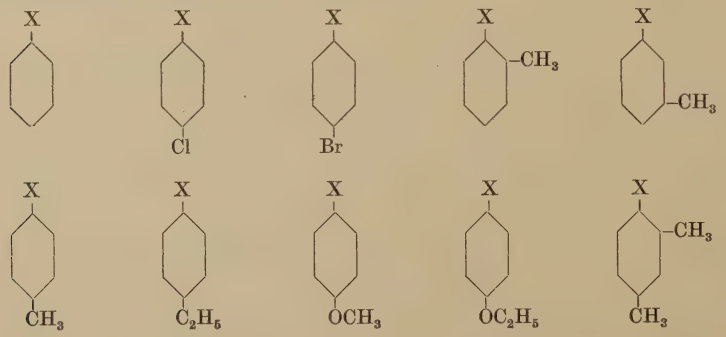
The largest class of arylphosphinic acids is that of the type $RPO(OH)_2$. These compounds are all solids and may be nitrated directly, the nitro-group entering the ring in the *meta*-position to the phosphorus. Reduction of the nitro-acids yields the corresponding amino-acids. Those acids containing halogen substituted in the benzene neucleus can be prepared from halogenated arylphosphines or by direct halogenation ; the halogen enters the ring in the para-position to the methyl group in the case of the *ortho*- and *meta*-tolylphosphinic acids. Carboxylic acids are obtained by oxidising phosphinic acids containing methyl groups with alkaline permanganate.

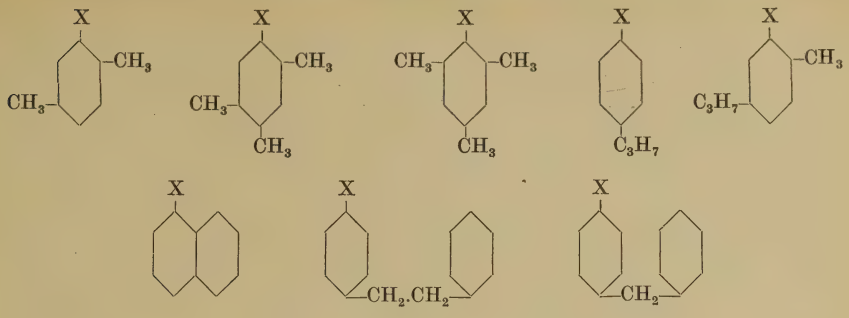
The acids of the type $R_2PO.OH$ are solids and capable of undergoing changes similar to those already described for the two preceding types. The type may be sub-divided as follows : $Ar_2PO.OH$, $AlkArPO.OH$, $ArAr'PO.OH$. The most numerous of these three classes is the first.

The following schemes show the principal acids dealt with in this section :—

Acids of the Type $RP(OH)_2$.

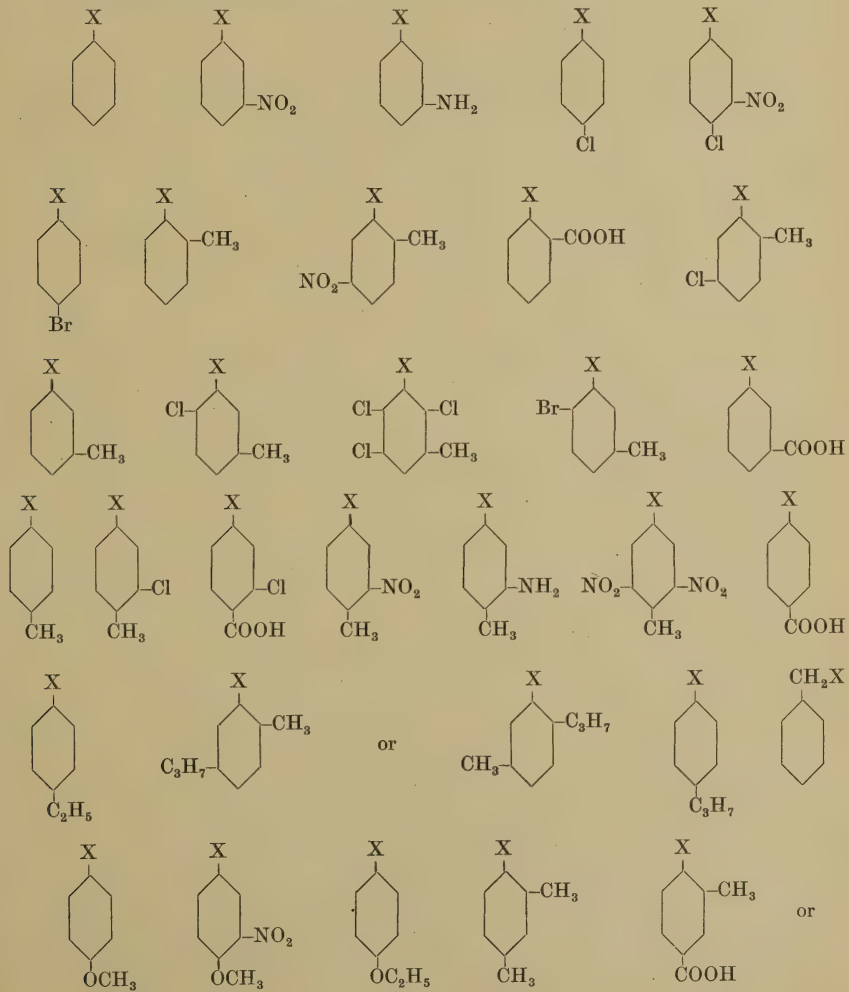
X represents the grouping $—P(OH)_2$.

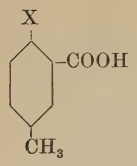
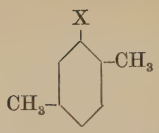
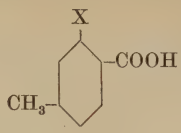


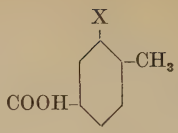
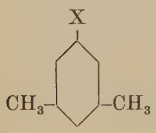
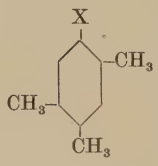
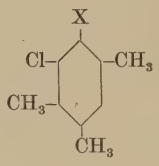
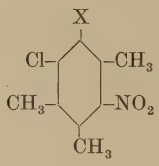
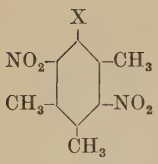
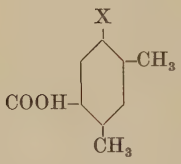
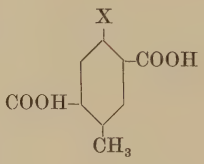
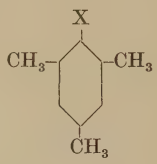
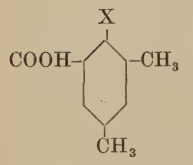
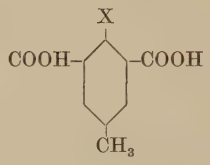


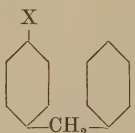
Acids of the Type $RPO(OH)_2$.

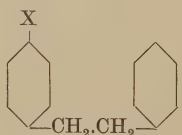
X represents the grouping $—PO(OH)_2$.



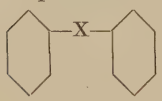
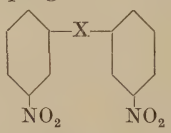
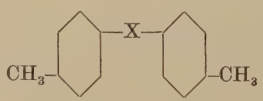
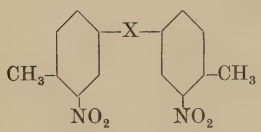
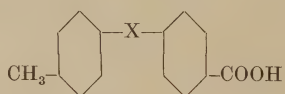












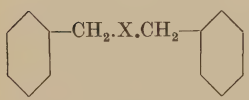
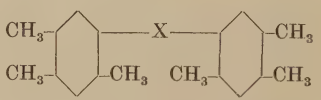
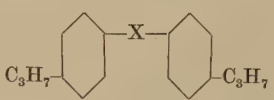
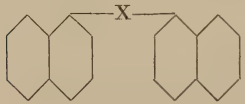
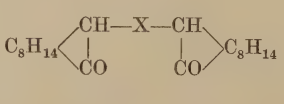
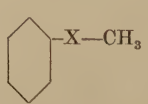


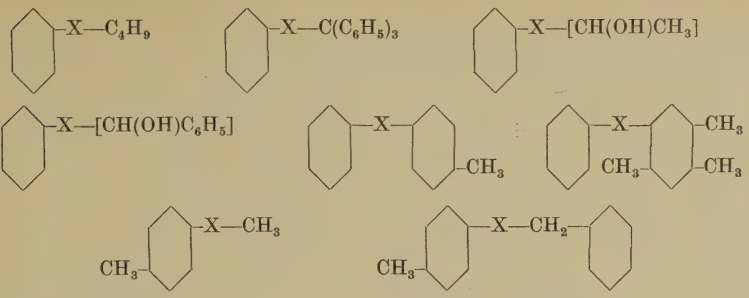


Acids of the Types $Ar_2PO.OH$, ArAr'PO.OH *and* AlkArPO.OH.

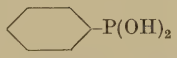
X represents the grouping —PO.OH.



Phenylphosphinous acid or *Phosphenylous acid*,[1]



This acid is most readily obtained by the action of water or warm alcohol on phenyldichlorophosphine :

$$C_6H_5.PCl_2 + 2H_2O = C_6H_5.P(OH)_2 + 2HCl$$

If alcohol is used, ethyl chloride is formed instead of hydrochloric acid. The preparation of triphenylphosphine by the Fittig reaction yields phenylphosphinous acid as a by-product.

Phenylphosphinous acid crystallises in white plates, M.pt. 70° C., is easily soluble in hot water or alcohol, but not very stable in air. When strongly heated it decomposes according to the equation

$$3C_6H_5.P(OH)_2 = C_6H_5.PH_2 + 2C_6H_6 + 2HPO_3$$

Treatment of the acid with mercuric chloride or sulphur dioxide oxidises it to phenylphosphinic acid. The following derivatives are formed by the combination of equimolecular proportions of the component substances : *Phenylphosphinous acid phenylhydrazine*, long, colourless prisms, M.pt. 135° C., soluble in hot water, sparingly soluble in cold water, and eliminating the acid portion of the molecule with excess of mineral acid ; *phenylphosphinous acid p-tolylhydrazine*, fine needles, M.pt. 148° C. ; *phenylphosphinous acid benzylhydrazine*, colourless prisms, M.pt. 108° C.

The following salts of phenylphosphinous acid are known : *potassium salt* ($2H_2O$), *ammonium salt*, *calcium salt*, *barium salt* ($4H_2O$), *lead salt* and *iron salt*.

Diethyl phenylphosphinite, $C_6H_5.P(OC_2H_5)_2$,[2] is formed when phenyldichlorophosphine reacts with sodium ethoxide ; it is a colourless, mobile liquid, B.pt. 235° C., density 1·032 at 16° C., insoluble in water ; in contact with ethyl iodide it isomerises to *ethyl phenylethylphosphinate*, $(C_2H_5)(C_6H_5)PO.OC_2H_5$.

Dithioethyl phenylphosphinite, $C_6H_5.P(SC_2H_5)_2$,[3] occurs when ethyl mercaptan (1 mol.) in ether solution is treated with sodium and phenyldichlorophosphine (0·5 mol.). It boils at 143° to 144° C. at 3·5 mm., and has a density of 1·1417 at 0° C. With *cuprous bromide*

[1] Michaelis and Ananoff, *Ber.*, 1874, 7, 1688; Michaelis, *Annalen*, 1876, 181, 265; Köhler and Michaelis, *Ber.*, 1877, 10, 807, 816; Michaelis and Soden, *Annalen*, 1885, 229, 295.

[2] Köhler and Michaelis, *Ber.*, 1877, 10, 816; Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 395.

[3] Arbusoff and Kamai, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 2037.

it forms a crystalline *compound*. At 150° C. it combines with *sulphur* yielding a *compound* $C_{10}H_{15}S_3P$, B.pt. 191° to 192° C. at 3·5 mm., density 1·2201 at 0° C.; this product is hydrolysed by sodium ethoxide to the crystalline salt $C_6H_5.PS(SC_2H_5)ONa$. When dithioethyl phenylphosphinite is heated at 130° C. with ethyl iodide in a sealed tube, it undergoes isomerisation to the *sulphide* $C_6H_5.P(C_2H_5)(SC_2H_5) : S$, B.pt. 169° to 170° C. at 3·5 mm., density 1·1693 at 0° C., which, with sodium ethoxide, yields the crystalline *sodium salt* of *phenylethylmonothiophosphinic acid*, $C_6H_5.P(C_2H_5)(ONa) : S$; the corresponding acid is only a syrup. Dithioethyl phenylphosphinite and benzyl chloride at 200° C. afford the compound $[S : P.C_6H_5(CH_2.C_6H_5)S.]_2$(?), M.pt. 145° to 146° C., and the oily compound $S : P.C_6H_5(CH_2.C_6H_5)SC_2H_5$, B.pt. 210° to 218° C. at 3 mm., density 1·1826 at 0° C.

Dithio-isobutyl phenylphosphinite, $C_6H_5.P(SC_4H_9)_2$, is prepared in a similar manner to the foregoing dithioethyl compound. It boils at 191° to 192° C. at 12·5 mm., and has a density of 1·0637. With flowers of sulphur it yields the *sulphide* $C_6H_5.P(SC_4H_9)_2 : S$, and with bromacetic acid it gives a crystalline *sodium salt*, $C_6H_5.P(:S)(ONa)CH_2.CO_2Na$, the corresponding free acid being non-crystallisable. Dithio-*iso*butyl phenylphosphinite with ethyl β-iodopropionate gives the compound $C_{13}H_{19}O_2S_2P$, B.pt. 200° to 206° C. at 4·5 mm., but hydrolysis does not afford a crystalline acid. Benzyl chloride at 210° C. gives a compound $S : P.C_6H_5(CH_2.C_6H_5)SC_4H_9$, M.pt. 145° to 146° C., and hydrolysis of the residue from the preparation of this compound yields *phenylbenzylmonothiophosphinic acid*, $S : P.C_6H_5(CH_2.C_6H_5)OH$, M.pt. 173° to 174° C.

Phenylphosphoneacetic acid, $HOP(C_6H_5)O.CH_2.CO_2H$.[1]—The *ethyl ester* of this acid is prepared by the interaction of di-*iso*butyl phenylphosphinite and ethyl monobromacetate; it boils at 195° to 198° C. at 7 mm., and has a density of 1·1223 at 0° C. The free acid melts at 121·5° to 122·5° C.; its *alkaloidal salts* cannot be resolved into optically active components.

Phenyl-α-phosphonepropionic acid, $HOP(C_6H_5)O.CH(CH_3)CO_2H$.—When ethyl α-bromopropionate is used in the foregoing condensation, *ethyl phenyl-α-phosphone propionate* is formed, B.pt. 191° to 193° C. at 7 mm., density 1·10535 at 0° C., the free acid melting at 168° to 169° C.

p-Chlorophenylphosphinous acid,[2]

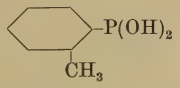
crystallises from water in fine, silky needles, and from alcohol in glistening plates or spears, M.pt. 130° to 131° C. The *ammonium*, *barium* (H_2O) and *copper* ($4H_2O$) *salts* are known. The *double salt* with *phenylhydrazine* crystallises in bright yellow plates or golden-yellow needles from dilute solution and melts at 169° C.

p-Bromophenylphosphinous acid,[3]

[1] Arbusoff and Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 1599.
[2] Michaelis, *Annalen*, 1896, 293, 222; Maecker, *Inaug. Dissert. Rostock*, 1893.
[3] Gundermann, *Inaug. Dissert. Rostock*, 1894.

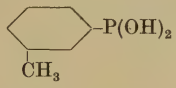
forms large, glistening, white plates, M.pt. 143° C., soluble in the usual organic solvents, less soluble in ether. The *potassium*, *ammonium*, *calcium*, *barium* ($4H_2O$), *lead*, *copper* and *aniline salts* are known.

o-Tolylphosphinous acid,[1]



is a non-crystalline compound, but capable of yielding salts. Its *calcium salt* crystallises in glistening plates containing a molecule of water of crystallisation.

m-Tolylphosphinous acid,



is a syrup having similar properties to the preceding compound.

p-Tolylphosphinous acid,[2]

separates as transparent, quadratic plates, M.pt. 104° to 105° C., stable in air and partially oxidised to the corresponding phosphinic acid when boiled with nitric acid. Its *copper salt* crystallises with four molecules of water in blue plates. The *ethyl ester* is a clear liquid, B.pt. 280° C., formed by the action of sodium alcoholate on *p*-tolyl-dichlorophosphine, and water decomposes it into its components. The *double compound* with *phenylhydrazine* crystallises in fine needles, M.pt. 161° C.

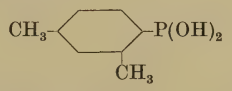
p-Ethylphenylphosphinous acid,[3]

readily crystallises from water and melts at 63° to 64° C., the *phenylhydrazine salt* melting at 133° C.

p-Anisylphosphinous acid,[4]

yields thin, silky needles, M.pt. 112° C.; its *lead salt* crystallises in glistening satin scales and the *phenylhydrazine salt* in pearly plates, M.pt. 116° C. *p-Phenetylphosphinous acid* forms white, glistening plates, M.pt. 115° C.

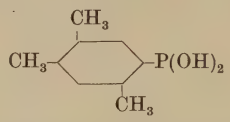
m-Xylylphosphinous acid,[5]



[1] Michaelis and Paneck, *Annalen*, 1882, **212**, 223.
[2] Michaelis and Paneck, *loc. cit.*; *Ber.*, 1880, **13**, 653.
[3] Michaelis, *Annalen*, 1896, **293**, 315; Lewschinski, *Inaug. Dissert. Rostock*, 1893.
[4] Michaelis, *loc. cit.*, p. 258.
[5] Michaelis and Paneck, *Annalen*, 1882, **212**, 237.

crystallises in colourless needles, M.pt. 97° to 98° C., soluble in alcohol. *p-Xylylphosphinous acid* has been isolated, but no details have been given.[1]

Pseudocumylphosphinous acid,[2]

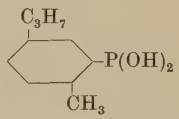


melts at 128° C. and forms crystals belonging to the rhombic system; the *phenylhydrazine salt* separates as white, silky needles, M.pt. 180° C. *Mesitylphosphinous acid* forms white needles, M.pt. 147° C., stable in air, the *phenylhydrazine salt* giving plates, melting with decomposition at 132° C.[3]

Cumylphosphinous acid,

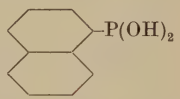
is a thick oil, yielding a crystalline *phenylhydrazine salt*, M.pt. 161° C.

Cymylphosphinous acid,



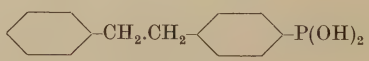
is isolated as an oil, the *barium salt* of which crystallises with one molecule of water.

α-Naphthylphosphinous acid,[4]



Mercury di-α-naphthyl and an excess of phosphorus trichloride are heated together in a sealed tube for three to five days at 180° to 200° C. The excess trichloride is then distilled off and the viscous residue treated with water and boiled until hydrogen chloride ceases to be evolved. A slight excess of sodium carbonate is then added and the solution filtered, the phosphinous acid being precipitated from the filtrate by acidifying. Purification is effected by recrystallisation from hot water, the insoluble product being di-α-naphthylphosphinous acid. α-Naphthylphosphinous acid forms small, warty groups of white needles, M.pt. 125° to 126° C., density 1·377,[5] very soluble in alcohol, less soluble in hot water, insoluble in dilute hydrochloric acid. When the acid is boiled with aqueous silver nitrate, metallic silver is deposited.

Dibenzylphosphinous acid,[6]



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[1] Weller, *Ber.*, 1888, 21, 1492.

[2] Michaelis, *Annalen*, 1897, 294, 4; Rothe, *Inaug. Dissert. Rostock*, 1892; Uster, *ibid.*, 1896.

[3] Hecker, *ibid.*, 1893.

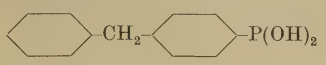
[4] Kelbe, *Ber.*, 1878, 11, 1499.

[5] Schroeder, *Ber.*, 1879, 12, 561.

[6] Michaelis, *Annalen*, 1901, 315, 50.

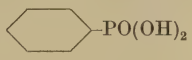
forms pearly plates, M.pt. 156° to 157° C., and yields well-crystallised salts.

Diphenylmethanephosphinous acid,[1]



is best crystallised from alcohol ; it melts at 84° C. It is very sparingly soluble in hot water. Its alcohol solution with an excess of sodium hydroxide yields the *sodium salt* as a thick, white precipitate. The *potassium*, *ammonium*, *calcium*, *lead* and *barium salts* are known, the last-named containing three molecules of water. The *double salt* with *phenylhydrazine* is sparingly soluble in water and melts at 171° C.

Phenylphosphinic acid or *Phosphenylic acid,*



may be isolated by several methods : (1) By treating the corresponding tetrahalides or oxyhalides with water : [2]

$$C_6H_5.PCl_4 + H_2O = C_6H_5.POCl_2 + 2HCl$$
$$C_6H_5.POCl_2 + 2H_2O = C_6H_5.PO(OH)_2 + 2HCl$$

(2) By treating the compound $C_6H_5.P=POH$ with nitric acid.[3] (3) By the action of concentrated nitric acid on phosphobenzene, $C_6H_5.P=P.C_6H_5$; if dilute nitric acid be used only phenylphosphinous acid results.[4] (4) The acid is formed when the sulphochloride, $C_6H_5.PSCl_2$, is boiled for a prolonged period with water.[5]

Phenylphosphinic acid crystallises in colourless, rhombic plates, M.pt. 158° C., density 1·475.[6] At 250° C. it decomposes into benzene and metaphosphoric acid, but if slowly heated to 200° C. two molecules of acid combine with the elimination of a molecule of water, and at 210° C. three molecules of acid lose two molecules of water. Heating with bromine and water in a sealed tube at 100° C. decomposes the acid, giving *p*-dibromobenzene, phosphoric acid and hydrogen bromide,[7] whilst heating with soda lime yields benzene and phosphoric acid.[8] When dry phenylphosphinic acid is heated in a reflux apparatus with the oxychloride, $C_6H_5.POCl_2$, phenylphosphinoxide results, $C_6H_5.PO_2$.[9] Phenylphosphinic acid forms the following salts, the water of crystallisation being indicated in brackets : *potassium salt*, *sodium salt* ($12H_2O$), *calcium salt* ($2H_2O$), *zinc salt*, *copper salt*, *silver salt*, *iron salt* ($2\frac{1}{2}H_2O$) ; also acid salts of *potassium*, *calcium* and *strontium*. When the silver salt is heated under reflux with ethyl iodide, the *diethyl ester* results, $C_6H_5.PO(OC_2H_5)_2$. It is a viscous liquid, B.pt. 267° C., having an odour resembling that of mustard oil, and is heavier than water, in

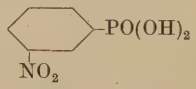
[1] Michaelis, *Annalen*, 1901, 315, 44.
[2] Michaelis and Mathais, *Ber.*, 1874, 7, 1070; Mathais, *Inaug. Dissert. Zürich*, 1875; Michaelis and Köhler, *Ber.*, 1876, 9, 519; Michaelis, *Ber.*, 1873, 6, 816.
[3] Michaelis, *Ber.*, 1875, 8, 499.
[4] Köhler and Michaelis, *Ber.*, 1877, 10, 807.
[5] Köhler and Michaelis, *Ber.*, 1876, 9, 1053.
[6] Schroeder, *Ber.*, 1879, 12, 561.
[7] Michaelis, *Annalen*, 1876, 181, 265.
[8] Michaelis and Benzinger, *Ber.*, 1876, 9, 517.
[9] Michaelis and Rothe, *Ber.*, 1892, 25, 1747.

which it is slightly soluble without decomposition.[1] The corresponding *dimethyl ester* boils at 247° C.[2] Decomposition of the tetrachloride, $C_6H_5.PCl_4$, by alcohol gives rise to a *monoethyl ester*, $C_6H_5.PO(OH)(OC_2H_5)$, a liquid decomposed by water. If the tetrachloride be heated with phenol, hydrogen chloride is evolved and the *diphenyl ester* is formed :[3]

$$C_6H_5.PCl_4 + 3C_6H_5OH = C_6H_5.PO(OC_6H_5)_2 + 3HCl + C_6H_5Cl$$

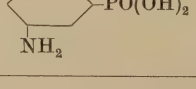
This ester forms white needles, M.pt. 63·5° C., readily soluble in alcohol, ether or benzene, insoluble in water. It is decomposed by alcoholic sodium hydroxide, but not by the aqueous alkali. The diphenyl ester also results when one molecular equivalent of the oxychloride, $C_6H_5.POCl_2$, is treated with two equivalents of phenol, but the use of one equivalent of the latter leads to the production of an *ester oxychloride*, $C_6H_5.POCl(OC_6H_5)$, which decomposes with water to form the corresponding *acid*, $C_6H_5.PO(OH)(OC_6H_5)$. The latter compound crystallises in fine needles, M.pt. 57° C., readily soluble in alcohol, ether, benzene or alkali, sparingly soluble in water. Its *ammonium salt* is anhydrous and forms colourless needles ; the *silver salt* separates from hot water in silky, glistening needles.

m-Nitrophenylphosphinic acid,[4]



Phenylphosphinic acid and fuming nitric acid in the proportion of 1 to 7 parts are heated together in a sealed tube for several hours at 100° to 105° C. and the reaction mixture then evaporated to dryness on the water-bath. The crude acid, after solution in water, is treated with pure barium carbonate, the mixture well shaken, filtered, and the residue washed with water until no barium ions are detected in the washings. The barium salt of the nitro-acid dissolves, whilst the barium salt of any unchanged phenylphosphinic acid remains behind. Evaporation of the filtrate yields yellow glistening plates of the barium salt, from which the free acid is liberated by sulphuric acid, the solution filtered and evaporated to dryness. Extraction of the residue with alcohol-free ether and removal of the solvent gives the free acid in white, concentric groups of needles, M.pt. 132° C., exploding above 200° C., easily soluble in water, alcohol or ether, insoluble in benzene and deliquescent in air. A *neutral barium salt* and an *acid barium salt* are known, both containing two molecules of water; the *calcium salt* contains half a molecule of water, and the *silver* and *lead salts* are anhydrous.

m-Aminophenylphosphinic acid,[5]



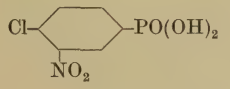
[1] Michaelis and Kammerer, *Ber.*, 1875, 8, 1306.
[2] Michaelis and Benzinger, *Ber.*, 1875, 8, 1310.
[3] Michaelis and Kammerer, *loc. cit.*; *Annalen*, 1876, 181, 337.
[4] Michaelis and Benzinger, *Ber.*, 1875, 8, 500, 1310; *Annalen*, 1877, 188, 276.
[5] Michaelis and Benzinger, *loc. cit.*; *Ber.*, 1876, 9, 513.

occurs when the preceding nitro-acid is reduced by tin and hydrochloric acid. It crystallises from hot water in fine needles, melting with decomposition at 280° C. When a hot solution of the amino-acid in nitric acid is treated with nitrous acid, a *diazonium nitrate* is obtained; this is deposited from water as white prisms, M.pt. 188° C., exploding at a higher temperature. At 130° C. the compound loses two molecules of water, and when heated with soda lime it yields aniline and phosphoric acid. It is a strong dibasic acid and forms two series of salts, of which the *barium* ($3H_2O$) and *silver salts* are red, and the *potassium* (H_2O) and *lead salts* are yellow. A *sodium salt* ($3H_2O$) and a *copper salt* are known.

p-Chlorophenylphosphinic acid,[1]

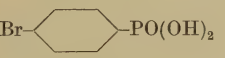
This acid is prepared by treating the corresponding tetrachloride or oxychloride with water. It separates from water in silky needles, or from alcohol in quadratic plates, M.pt. 184° to 185° C. The *acid barium salt* crystallises in bushy needles, the *acid silver salt* in glistening plates, whilst the *neutral silver salt* is an amorphous powder, which readily darkens when exposed to the light. The dry acid, heated with the oxychloride in benzene solution, yields *p*-chlorophenylphosphinoxide.

m-Nitro-p-chlorophenylphosphinic acid,[2]



occurs when the preceding compound is nitrated by fuming nitric acid. It crystallises either in pale yellow glistening plates or in long needles, M.pt. 166° to 168° C., soluble in water, alcohol or ether, but insoluble in benzene. The *alkali salts* form yellow needles, readily soluble in water, whilst the *alkaline earth salts* are sparingly soluble. Reduction of the acid by tin and hydrochloric acid gives a 43 per cent. yield of the *amino-acid*, which melts with decomposition at 270° C. and becomes discoloured in air.

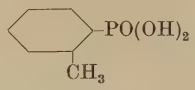
p-Bromophenylphosphinic acid,



forms long needles, M.pt. 202° C., above which temperature it decomposes into bromobenzene and phosphoric acid. Nitration yields *m-nitro-p-bromophenylphosphinic acid*, consisting of bright yellow plates, M.pt. 185° C., exploding on strong heating. An isomeric bromophenylphosphinic acid has also been obtained from the aluminium chloride residue obtained in the preparation of *p*-bromophenylphosphine; it melts at 265° C. and is distinguished from the *para*-bromo-derivative by its insolubility in ether.

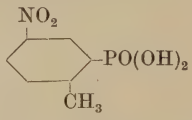
[1] Michaelis, *Annalen*, 1896, **293**, 228.
[2] Michaelis, *loc. cit.*; Eifler, *Inaug. Dissert. Rostock*, 1894.

o-Tolylphosphinic acid,[1]



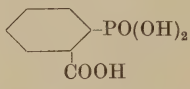
prepared in the usual manner, forms small, granular crystals, M.pt. 141° C., and when strongly heated is decomposed into toluene and phosphoric acid. The following salts are known: *ammonium salt*, *acid barium salt* (H_2O), *copper salt*, *lead salt* and *anilide*, the last-named forming white needles, M.pt. 234° C.

5-Nitro-o-tolylphosphinic acid,



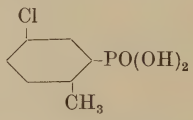
When the previous acid is evaporated on the water-bath with seven parts of fuming nitric acid, nitration takes place in the *meta*-position to the phosphorus. The nitro-acid forms pale yellow needles, M.pt. 174° C., and is less soluble in water than the corresponding *para*-compound. The *barium* and *calcium salts* are yellow, microcrystalline powders. Reduction of the nitro-acid yields the *amino-acid* as brownish needles, softening at 280° to 300° C. and decomposing at higher temperatures; the *barium* and *calcium salts* are reddish-brown powders.

o-Carboxyphenylphosphinic acid,



15 grams of *o*-tolylphosphinic acid in 1,500 c.c. of water are treated with 27·6 grams of potassium permanganate, added in small portions, and the whole maintained at 50° C. for ten weeks. The resulting product forms small, white needles, M.pt. 172° C., readily soluble in water or alcohol, insoluble in ether or benzene. The crystals sublime unchanged. A white *silver salt* is known, which is affected by light. Treatment of the acid with phosphorus pentachloride gives the *acid chloride*, $ClCO.C_6H_4.POCl_2$, a crystalline mass, M.pt. 54° C.

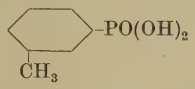
5-Chloro-o-tolylphosphinic acid,[2]



is obtained by direct chlorination of *o*-tolylphosphinic acid at the ordinary temperature. It forms small, compact crystals from dilute alcohol, M.pt. 205° C., readily soluble in water but reprecipitated by hydrochloric acid. Strong heating decomposes the acid, yielding *p*-chlorotoluene, which proves the constitution. Prolonged chlorination gives rise to a *dichloro-o-tolylphosphinic acid*, M.pt. 240° C.

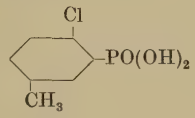
[1] Michaelis and Paneck, *Annalen*, 1882, *212*, 232; Michaelis, *ibid.*, 1896, *293*, 294.
[2] Michaelis, *loc. cit.*

m-Tolylphosphinic acid,[1]



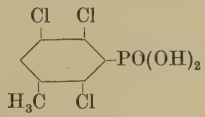
crystallises as white, glistening needles, M.pt. 116° to 117° C., easily soluble in water, alcohol or ether. It forms two series of *potassium* and *silver salts*, also a *neutral barium salt.*

6-Chloro-m-tolylphosphinic acid,



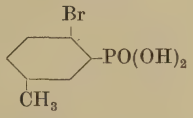
occurs when chlorine is passed for twenty minutes into an aqueous solution of *m*-tolylphosphinic acid. It forms white, feathery needles, M.pt. 176° C., above which temperature it decomposes into phosphoric acid and *p*-chlorotoluene, the formation of the latter compound proving the position of the chlorine in the ring. The *neutral silver salt* of the acid is a crystalline body, unaffected by light.

2 : 5 : 6-Trichloro-m-tolylphosphinic acid,



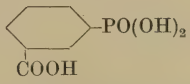
When the preceding chloro-acid in aqueous solution is chlorinated for three hours, the trichloro-acid is isolated in plates or needles, M.pt. 220° C. It sublimes above its melting-point and the crystals thus obtained separate from methyl alcohol as long, colourless needles, M.pt. 82° C. When decomposed, the trichloro-acid yields 2 : 4 : 5-trichlorotoluene, which proves its composition. The *silver salt* is a white powder, somewhat affected by light.

6-Bromo-m-tolylphosphinic acid,



occurs as white needles, M.pt. 198° C., when one molecular equivalent of bromine reacts with one equivalent of *m*-tolylphosphinic acid in aqueous solution. The *silver salt* is a white, amorphous powder. When the acid is heated above its melting-point it yields *p*-bromotoluene and metaphosphoric acid.

m-Carboxyphenylphosphinic acid,



obtained by the oxidation of *m*-tolylphosphinic acid with alkaline potassium permanganate at 50° C. during a period of ten days, crystallises

[1] Michaelis, *Annalen*, 1896, **293**, 305.

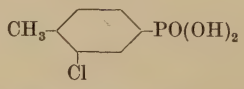
in white needles, M.pt. 245° to 246° C. When heated above its melting-point it yields benzoic acid. The *neutral silver salt* is a white, caseous precipitate, unaffected by light; the *lead* and *barium salts* are white flocculent precipitates. Phosphorus pentachloride converts the acid into the *acid chloride*, $ClCO.C_6H_4.POCl_2$, a white crystalline mass, M.pt. 61° C., B.pt. above 360° C.

p-Tolylphosphinic acid,[1]

is obtained by treating the corresponding tetrachloride with water. It separates from the latter solvent as matted, woolly needles, M.pt. 189° C., readily soluble in alcohol or ether. It is a strong dibasic acid, forming three series of salts: (*a*) containing acid of crystallisation, (*b*) acid salts, (*c*) neutral salts. The following are known: *potassium salt*, $C_7H_7.PO(OH)(OK).C_7H_7.PO(OH)_2$, glistening, colourless needles; *acid barium salt*, $[C_7H_7.PO(OH)O]_2Ba$, isolated as a glistening, crystalline precipitate; *acid calcium salt*, similar to the barium salt; *acid silver salt*, $C_7H_7.PO(OH)(OAg)$, white crystalline plates; and *neutral silver salt*, $C_7H_7.PO(OAg)_2$, a white, caseous precipitate. When an aqueous solution of the acid is warmed with bromine it decomposes as follows:—

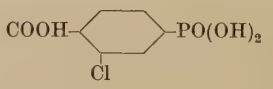
$$C_7H_7.PO(OH)_2 + Br_2 + H_2O = C_7H_7Br + PO(OH)_3 + HBr$$

3-Chloro-p-tolylphosphinic acid,[2]



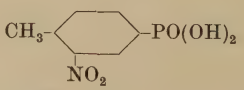
occurs when the corresponding oxychloride is treated with water. It forms pearly plates, M.pt. 190° C., readily soluble in hot alcohol. When heated with bromine and water it yields *o*-chloro-*p*-bromotoluene. It forms an *acid anilide*, M.pt. 216° C., and *silver* and *acid barium salts* are known.

3-Chloro-p-carboxyphenylphosphinic acid,



is prepared by oxidising the previous compound with alkaline permanganate solution at 50° to 60° C. It forms rhombic plates, M.pt. 254° C. Nitration with seven parts of fuming nitric acid gives a *mononitro-acid*, consisting of yellowish plates, M.pt. 200° C., above which temperature it explodes.

3-Nitro-p-tolylphosphinic acid,[3]



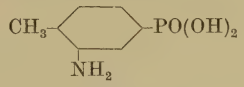
[1] Michaelis and Paneck, *Ber.*, 1880, 13, 653; *Annalen*, 1882, 212, 225; Michaelis and Lange, *Ber.*, 1875, 8, 1313; Michaelis, *Ber.*, 1879, 12, 1009.

[2] Melchiker, *Ber.*, 1898, 31, 2915; *Chem. Zentr.*, 1899, i, 129.

[3] Michaelis, *Annalen*, 1896, 293, 270; Piper, *Inaug. Dissert. Rostock*, 1893.

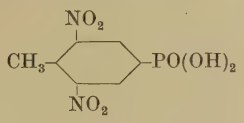
One part of *p*-tolylphosphinic acid and seven parts of fuming nitric acid are heated together on the water-bath for two hours, then evaporated to dryness and the residue treated with water, the nitrated acid going into solution. The acid is best purified by means of its barium salt, pale yellow, stellate groups of needles being obtained, M.pt. 191° C. The compound explodes when heated above its melting-point. The following salts are known: *barium salt*, $C_7H_6(NO_2)PO_3Ba.2H_2O$, yellow plates; *calcium salt*, $C_7H_6(NO_2)PO_3Ca.H_2O$, a pale yellow powder; *lead*, *copper* and *silver salts*, amorphous powders, the last-named being affected by light. When the silver salt is heated under reflux with ethyl iodide, the *diethyl ester*, $C_7H_6(NO_2)PO(OC_2H_5)_2$, is produced; this product has a faint pungent odour resembling that of mustard oil, and cannot be distilled without decomposition.

3-Amino-p-tolylphosphinic acid,



Reduction of 120 grams of the previous compound with zinc and hydrochloric acid gives only five grams of the pure amino-acid. The acid forms white, glistening needles, rapidly affected by air and decomposing at about 290° C. The *silver salt* is a white powder, sensitive to light; the *lead salt* is a yellow, amorphous powder, and the *diethyl ester* an undistillable liquid, having a mustard oil odour.

3 : 5-Dinitro-p-tolylphosphinic acid,



One part of *p*-tolylphosphinic acid, five parts of concentrated nitric acid and seven parts of fuming nitric acid are heated together for three hours on a water-bath, then poured into a large volume of water. The dinitro-acid is extracted from the solution by ether, from which solvent it crystallises in yellow plates, M.pt. 251° C., exploding on rapid heating. The *barium salt* crystallises with two molecules of water, the first of which is eliminated at 110° C. and the second with difficulty at 180° C.; the *lead salt* is a yellow, amorphous powder.

4-Carboxyphenylphosphinic acid,[1]

occurs when *p*-tolylphosphinic acid is oxidised by alkaline potassium permanganate solution at 50° C., the process taking several days for completion. The potassium salt thus isolated is evaporated at 50° C. with concentrated hydrochloric acid to obtain the free acid. The acid crystallises from hydrochloric acid in plates and from water in needles. The melting-point is above 300° C., strong heating causing decomposition with formation of benzoic acid, phosphoric acid and carbon. Unlike *p*-tolylphosphinic acid, this acid is not attacked by bromine in the presence of water at 130° C. The following salts are known:

[1] Michaelis and Paneck, *Ber.*, 1881, 14, 405; Michaelis, *loc. cit.*

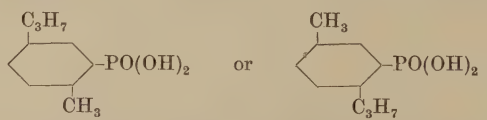
acid calcium salt, $[COOH.C_6H_4.PO(OH)O]_2Ca$, which on heating yields benzoic acid and calcium phosphate, showing that the calcium is not bound to the acid residue; *copper salt*, $Cu_3[OCO.C_6H_4.PO_3]_2.1\frac{1}{2}H_2O$, a pale blue crystalline precipitate; *silver salt*, $AgOCO.C_6H_4.PO(OAg)_2$; *potassium salt*, $KOCO.C_6H_4.PO(OH)_2$, fine needles, soluble in water, sparingly soluble in alcohol. When the foregoing potassium salt is heated with acetic acid, or hydrochloric acid is added to its aqueous solution, a sparingly soluble *potassium salt*, $KOCO.C_6H_4.PO(OH)_2.HOCO.C_6H_4.PO(OH)_2$, separates in bushy columns; the corresponding *sodium salt* is non-crystalline. Barium and ferric chlorides give precipitates with the free acid. When the silver salt is refluxed with methyl iodide, the *methyl ester*, $CH_3OCO.C_6H_4.PO(OCH_3)_2$, is obtained as a liquid which cannot be distilled without some decomposition. When finely powdered *p*-carboxyphenylphosphinic acid dissolved in absolute alcohol is saturated with dry hydrogen chloride, an *acid ethyl ester* is formed, $C_2H_5OCO.C_6H_4.PO(OH)_2$, together with some *neutral ester*. After removing the solvent, the liquid is dried and stirred until it solidifies. This mixture of esters is then dissolved in water and shaken with silver nitrate, the resulting curdy precipitate being washed, suspended in distilled water, dissolved by adding the minimum amount of nitric acid and the silver removed by the addition of hydrochloric acid. The filtrate is evaporated, when the acid ethyl ester separates in needles, M.pt. 78° C., readily soluble in water or alcohol. The *acid silver salt* of this ester, $C_2H_5OCO.C_6H_4.PO(OH)(OAg)$, crystallises in snow-white crystalline spangles. *p*-Carboxyphenylphosphinic acid also yields an *acid chloride*, $ClCO.C_6H_4.POCl_2$, when treated with phosphorus pentachloride. This melts at 83° C. and boils at 315° C. It is decomposed by hot water, giving the free acid, by ammonium hydroxide, forming the *amide*, and by alcohol, yielding a mixture of neutral and acid esters. Phosphorus pentachloride at 200° C. removes the phosphorus as follows :—

$$ClCO.C_6H_4.POCl_2 + PCl_5 = ClC_6H_4.COCl + POCl_3 + PCl_3$$

p-Ethylphenylphosphinic acid,[1]

forms white, glistening, matted needles, M.pt. 164° C., easily soluble in alcohol, ether or hot water, insoluble in benzene. It forms an *acid ammonium salt*, a *phenylhydrazine salt*, a *potassium salt*, $C_8H_9.PO_3HK.C_8H_9.PO_3H_2$, a *barium salt*, $C_8H_9.PO_3Ba.3H_2O$, a *copper salt*, crystallising with a molecule of water, and a white *silver salt*. Oxidation of the acid by potassium permanganate yields 4-carboxyphenylphosphinic acid.

Cymylphosphinic acid or *Methylisopropylphenylphosphinic acid*,[2]



is a liquid forming two *silver salts*, $C_{10}H_{13}PO_3HAg$ and $C_{10}H_{13}PO_3Ag_2$,

[1] Michaelis, *Annalen*, 1896, **293**, 317. [2] Michaelis, *Annalen*, 1897, **294**, 54.

also a *phenylhydrazine salt*, M.pt. 156° C., which crystallises in warty plates. Oxidation by alkaline potassium permanganate yields *methyl-oxyisopropylphenylphosphinic acid*, $CH_3.C_6H_3[C(OH)(CH_3)_2]PO(OH)_2$, as an oil.

Cumylphosphinic acid,

crystallises from carbon disulphide in small needles, and from cumene in small rhombic crystals, M.pt. 139° C., readily soluble in water, less soluble in alcohol or ether. The *barium salt* is a white, crystalline powder; the *silver salt* is readily decomposed and is affected by light; the *phenylhydrazine salt* forms pale yellow plates, M.pt. 172° C., moderately soluble in water, alcohol or ether. The acid also forms a stable, golden-yellow *salt* with *aminoazobenzene*, which crystallises in plates, M.pt. 185° C. When 4 grams of cumylphosphinic acid are oxidised with 2 grams of potassium permanganate, *oxyisopropylphenylphosphinic acid* is formed, $(CH_3)_2C(OH)C_6H_4.PO(OH)_2$; this is an oil, soluble in ether, alcohol or water, insoluble in dilute hydrochloric acid; when heated at 105° to 120° C. it decomposes, yielding a white powder, analysis of which agrees with the composition of *allylphenylphosphinic acid*, $C_3H_5.C_6H_4.PO(OH)_2$.

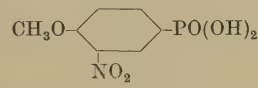
Benzylphosphinic acid,[1]

10 grams of phosphonium iodide and 5 grams of benzaldehyde are digested together at 100° C. for four to five hours, phosphine and hydrogen iodide being evolved. When the brown reaction product is warmed with water, a white crystalline mass results, consisting of a mixture of dibenzylphosphinic acid and tribenzylphosphine oxide, and benzylphosphinic acid remains in solution. The crude product from the solution crystallises from acetic acid in shining, stellate groups of prisms, M.pt. 169° C., soluble in alkalis, but insoluble in the usual organic solvents. It turns blue litmus red, liberates carbon dioxide from carbonates, and forms a *silver salt*, $C_7H_7.PO_3Ag_2$. Nitration of the acid gives a nitro-acid, probably *3-nitrobenzylphosphinic acid*, $NO_2.C_6H_4.CH_2.PO(OH)_2$, which crystallises in shining yellow needles, melting at about 217° C.

p-Anisylphosphinic acid,[2]

forms large, rhombic crystals, M.pt. 158° C., fairly soluble in water or alcohol, insoluble in ether. The *potassium salt* separates in plates containing four molecules of water; the *barium* and *silver salts* are white, and the *iron salt*, $(CH_3O.C_6H_4.PO_3)_3Fe_2.3H_2O$, is a yellow amorphous powder.

3-Nitro-4-methoxyphenylphosphinic acid,



[1] Litthauer, *Ber.*, 1889, **22**, 2144.

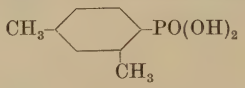
[2] Michaelis, *Annalen*, 1896, **293**, 251.

probably represents the structure of the acid formed when the preceding compound is nitrated. It forms colourless, matted needles, M.pt. 187° C., exploding at higher temperatures. The *acid barium salt*, $[(CH_3O)NO_2.C_6H_3.PO_3H]_2Ba.3H_2O$, yields yellow, rhombic crystals ; the *copper salt* is a greenish-blue powder, and the *basic cobalt salt*, $(CH_3O)NO_2.C_6H_3.PO_3Co_2O$, is a reddish-brown powder.

p-Phenetylphosphinic acid,

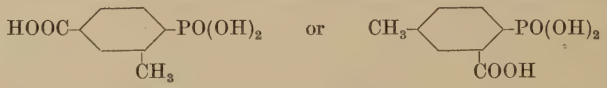
forms white needles, M.pt. 165° C., readily soluble in alcohol or water, and giving a white *silver salt.*

m-Xylylphosphinic acid or 2 : 4-*Dimethylphenylphosphinic acid*,[1]



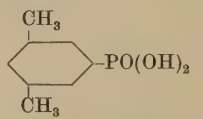
This compound is obtained from the corresponding tetrachloride, the latter being isolated from *m*-xylyldichlorophosphine, derived from the products of reaction between *m*-xylene, phosphorus trichloride and aluminium chloride. The acid is said to give two distinct crops of crystals, M.pts. 194° C. and 161° C., designated α and β respectively. If this statement be correct, the foregoing Friedel-Crafts reaction gives rise simultaneously to 1 : 2 : 4- and 1 : 3 : 5-xylyldichlorophosphines, the 1 : 2 : 4-compound being designated α and the 1 : 3 : 5-derivative designated β. The 2 : 4-dimethyl-compound crystallises in white needles, M.pt. 194° C., readily soluble in hot water or alcohol, sparingly soluble in ether. Heating with alkali gives *m*-xylene and phosphoric acid. The *barium*, *cadmium* and *nickel salts* all crystallise with one molecule of water, whilst the *silver salt* is anhydrous. Nitration of the acids yields two *nitro-acids*, one melting at 182° C. and sparingly soluble, the second melting at 107° C. and readily soluble in the usual solvents.

2 (or 4)-Carboxy-4 (or 2)-methylphenylphosphinic acid,



occurs when the preceding acid is oxidised at 50° to 60° C. with the requisite quantity of alkaline permanganate. It forms colourless prisms, M.pt. 262° C., further heating giving phosphoric and toluic acids. The acid is tribasic, and its salts are difficult to purify. Phosphorus pentachloride converts it into an *acid chloride*, $ClCO.C_6H_3(CH_3)POCl_2$, a viscous liquid, faintly fuming in air and boiling at 310° C.

3 : 5-Dimethylphenylphosphinic acid,

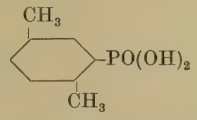


is obtained as described under *m*-xylylphosphinic acid. It crystallises in plates or needles, M.pt. 161° C., more readily soluble in water than its isomeride. The *nitro-acid* melts at 107° C., and is difficult to purify. Oxidation gives *3* (or *5*)-*carboxy-5* (or *3*)-*methylphenylphosphinic acid*,

[1] Weller, *Ber.*, 1887, **20**, 1718; 1888, **21**, 1492.

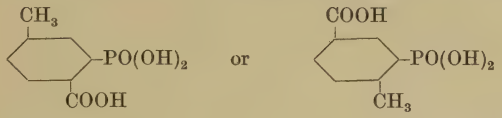
melting at 220° C., the *acid chloride* of which is a viscous oil, B.pt. 249° C. at 147 mm.

p-Xylylphosphinic acid,[1]



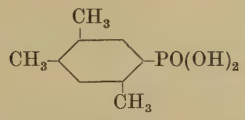
forms colourless needles, M.pt. 179° to 180° C., moderately soluble in water, readily soluble in alcohol. When heated above its melting-point it is decomposed into *p*-xylene and phosphoric acid. The *acid potassium salt*, $(CH_3)_2C_6H_3.PO_3HK$, and the *barium salt*, $(CH_3)_2C_6H_3.PO_3Ba$, both form white, pearly plates. Nitration yields a *mononitro-acid*, consisting of colourless needles, M.pt. 224° C., exploding on strong heating.

2 (or **5**)**-Carboxy-5** (or **2**)**-methylphenylphosphinic acid,**



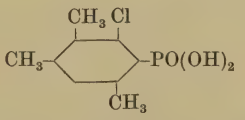
occurs when the preceding compound is oxidised by alkaline permanganate. It forms slender yellow needles, M.pt. 278° C., heating above this temperature causing decomposition into *p*-toluic and phosphoric acids. Phosphorus pentachoride converts it into the *acid chloride*, $(ClCO.C_6H_3.CH_3)POCl_2$, a colourless, crystalline mass, fuming in air.

Pseudocumylphosphinic acid or *2 : 4 : 5-Trimethylphenyl-phosphinic acid,*[2]



Decomposition of the corresponding tetrachloride by water yields the acid as white, glistening plates or long, colourless needles, M.pt. 212° C., readily soluble in hot water or dilute alcohol, insoluble in benzene. Bromine in the presence of water gives phosphoric acid and tribromo*pseudo*cumene, while chlorine has a similar action, except that traces of the chloro-acid (*vide infra*) also occur. The *acid potassium salt*, $C_9H_{11}.PO_3HK$, forms white, matted needles; the *acid barium salt*, $(C_9H_{11}.PO_3H)_2Ba$, crystallises in glistening needles; the *acid nickel salt*, $(C_9H_{11}.PO_3H)_2Ni.4H_2O$, separates as bright green, glistening plates; and the *neutral silver salt*, $C_9H_{11}.PO_3Ag_2$, is a white, caseous precipitate.

6-Chloro-2 : 4 : 5-trimethylphenylphosphinic acid,

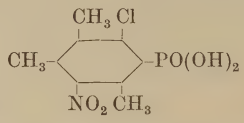


[1] Michaelis and Paneck, *Annalen*, 1882, **212**, 238; *Ber.*, 1880, **13**, 653; Weller, *Ber.*, 1888, **21**, 1492.

[2] Michaelis, *Annalen*, 1897, **294**, 7; Rothe, *Inaug. Dissert. Rostock*, 1892; Uster, *Inaug. Dissert. Rostock*, 1896.

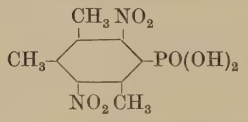
The preceding acid in acetic acid solution is chlorinated until a test portion does not give a clear solution in sodium hydroxide, this indicating that decomposition is taking place into phosphoric acid and chlorinated *pseudo*cumene. The solution is then evaporated to dryness, the residue treated with ammonium hydroxide, the liquid filtered and the acid precipitated from the filtrate by the addition of hydrochloric acid. Recrystallisation from alcohol and then acetic acid gives white needles, M.pt. 235° C., readily soluble in alcohol, ether or boiling acetic acid, sparingly soluble in boiling water. The *acid phenylhydrazine salt* forms small needles from alcohol, M.pt. 197·5° C.

6-Chloro-3-nitro-2 : 4 : 5-trimethylphenylphosphinic acid,



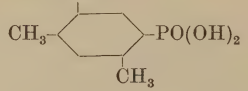
occurs when the preceding compound is added to strongly cooled fuming nitric acid and the solution poured into water. After filtering and saturating the solution with ammonia, lead acetate is added to precipitate the *lead salt*. This is filtered off, washed with cold water, suspended in alcohol slightly acidified with hydrochloric acid, and treated with hydrogen sulphide. The lead sulphide is removed, the filtrate evaporated to dryness and the residue recrystallised from cold water. Long flat needles of the acid are deposited, M.pt. 227° to 228° C., exploding on rapid heating and readily dissolving in the usual organic solvents.

3 : 6-Dinitro-2 : 4 : 5-trimethylphenylphosphinic acid,



*Pseudo*cumylphosphinic acid is dissolved in cold fuming nitric acid ; a violent reaction occurs, and after twelve hours the excess of nitric acid is evaporated off and the residue recrystallised from hot water. The dinitro-acid forms small white crystals melting with decomposition at 239° C., readily soluble in alcohol or ether, hot acetic acid or boiling chloroform, whilst the solution in ammonium hydroxide is very deep yellow. The acid is dibasic, and its salts, which are as follows, are not decomposed by dilute acetic acid : *acid phenylhydrazine salt*, small needles, M.pt. 240° C. ; *acid anilide*, glistening white needles, M.pt. 273° C. with decomposition ; *copper salt*, $C_9H_9(NO_2)_2PO_3Cu.H_2O$, small greenish needles ; *silver salt*, $C_9H_9(NO_2)_2PO_3Ag_2$, colourless needles, soon darkening in air ; *acid silver salt*, $C_9H_9(NO_2)_2PO_3HAg$, small white plates.

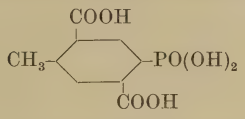
5-Carboxy-2 : 4-dimethylphenylphosphinic acid,



One molecular proportion of *pseudo*cumylphosphinic acid is partially oxidised by two molecular proportions of potassium permanganate

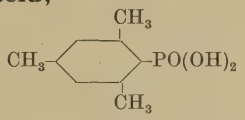
when the mixture is heated at 60° to 70° C. for twenty-four hours. The product is a white, spongy powder, M.pt. 258° C., soluble in alcohol, but sparingly soluble in cold water. When strongly heated it decomposes, yielding phosphoric acid and dimethylbenzoic acid ($COOH : CH_3 : CH_3 = 1 : 2 : 4$), M.pt. 126° C., which proves the structure of the phosphinic acid. The *silver salt* is a white powder, sensitive to light.

2 : 5-Dicarboxy-4-methylphenylphosphinic acid,



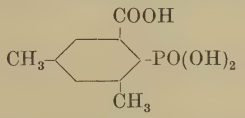
occurs when four molecular proportions of permanganate are used in the preceding preparation. The acid produced is a very hygroscopic yellow powder, M.pt. 185° to 190° C., and probably has the structure indicated.

Mesitylphosphinic acid,



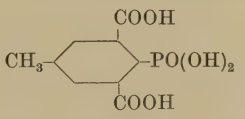
forms long transparent needles, M.pt. 167° C., sparingly soluble in cold water. When heated above its melting-point the acid gives phosphoric acid and mesitylene. It yields the following salts : *ammonium salt*, $C_9H_{11}.PO_3H(NH_4)$, fine, four-sided needles ; *barium salt*, small needles ; *silver salt*, white plates ; *nickel salt*, large green crystals containing eight molecules of water.

6-Carboxy-2 : 4-dimethylphenylphosphinic acid,



occurs as a white, amorphous powder, melting with decomposition at 245° C., readily soluble in alcohol, insoluble in ether. When heated above its melting-point it yields phosphoric acid and mesitylenic acid, M.pt. 166° C. The *silver salt*, $(CH_3)_2(COOAg)C_6H_2.PO(OAg)_2$, is white and affected by light. The above composition is assigned to the acid since the methyl group in the *para*-position to the phosphinic grouping does not appear to be oxidised before the other methyl groups in the ring judging from the case of *pseudo*cumylphosphinic acid, p. 117.[1]

2 : 6-Dicarboxy-4-methylphenylphosphinic acid,



sinters at 215° C. and melts at 255° C. It is a hygroscopic powder, giving phosphoric and uvitic acids on strong heating. The *silver salt* is a stable, white powder.

[1] Author.

α-Naphthylphosphinic acid,[1]

is obtained by heating mercury di-α-naphthyl and phosphorus trichloride together at 200° C., or by hydrolysis of the corresponding tetrachloride.[2] In the first method the melt, after filtering and treating with chlorine, is decomposed by water. The acid forms bushy needles, M.pt. 190° C., density 1·435,[3] yielding naphthalene and metaphosphoric acid on strong heating. The *silver salt* is soluble in ammonia and nitric acid.

Diphenylmethanephosphinic acid,[4]

forms long, colourless needles, M.pt. 196° C., heating above this temperature giving diphenylmethane and metaphosphoric acid. The following salts are known : *potassium salt*, *ammonium salt*, *barium salt* (H_2O), *cobalt salt* ($4H_2O$), *copper salt*, *lead salt*, *silver salt* and *phenylhydrazine salt*, M.pt. 187° C. Oxidation with permanganate gives the following derivative.

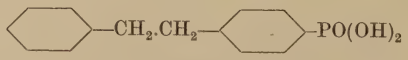
Benzophenonephosphinic acid,

occurs when the preceding compound is treated with alkaline potassium permanganate at 50° C. for ten days. It separates in pearly plates, M.pt. 204° C., readily soluble in alcohol, insoluble in water. Having ketonic as well as acidic properties, the acid forms a compound with phenylhydrazine, consisting of white plates, M.pt. 124° C. The *ethyl ester* is a viscous yellow oil, and forms an *oxime*. *Silver*, *ammonium* and *lead salts* are known. All these derivatives when strongly heated yield benzophenone and metaphosphoric acid. Phosphorus pentachloride reacts with the acid as follows :—

$$C_6H_5.CO.C_6H_4.PO(OH)_2 + 3PCl_5 = C_6H_5.C(Cl_2).C_6H_4.POCl_2 + 3POCl_3 + 2HCl$$

The *oxychlorophosphine* thus obtained forms a white, crystalline mass, M.pt. 64° C., B.pt. 258° C. at 15 mm., which soon decomposes in the air, and when gently warmed with water gives benzophenonephosphinic acid, the carbon-bound chlorine atoms being replaced by oxygen.

Dibenzylphosphinic acid,[5]



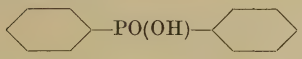
forms colourless plates, M.pt. 256° C., decomposing in the usual manner

[1] Kelbe, *Ber.*, 1876, 9, 1051.
[2] Lindner and Strecker, *Monatsh.*, 1929, 53 and 54, 274.
[3] Schroeder, *Ber.*, 1879, 12, 561.
[4] Michaelis, *Annalen*, 1901, 315, 45; Güsewell, *Inaug. Dissert. Rostock*, 1895.
[5] Michaelis, *Annalen*, 1901, 315, 50.

on heating and forming benzoic acid and *p*-carboxyphenylphosphinic acid on oxidation:

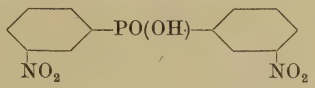
$$C_6H_5.CH_2.CH_2.C_6H_4.PO(OH)_2 + 5O = C_6H_5COOH + COOH.C_6H_4.PO(OH)_2 + H_2O$$

Diphenylphosphinic acid,[1]



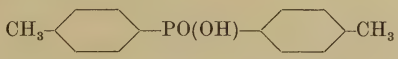
This acid is most readily produced by dissolving diphenylchlorophosphine in hydrochloric acid and boiling the solution with nitric acid. From hot concentrated nitric acid it crystallises in long, hair-like, snow-white needles, melting at about 190° C., density 1·331 ;[2] it also dissolves in alcohol, but is insoluble in water. The *silver salt* forms white silky needles from water.

3 : 3′-Dinitrodiphenylphosphinic acid,[3]

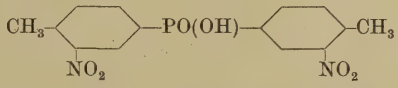


occurs when " mixed acid " reacts with diphenylphosphinic acid. The product is a yellow, amorphous powder, M.pt. 268° C., only sparingly soluble in the usual solvents. The *ammonium salt* forms small yellow columns, M.pt. 260° C., whilst the *potassium*, *barium* ($6H_2O$), *silver* and *lead salts* are also known. Reduction of the acid by tin and hydrochloric acid yields *3 : 3′-diaminodiphenylphosphinic acid*, consisting of small brown crystals decomposing at 276° C.

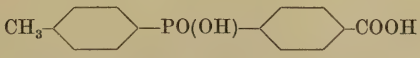
Di-p-tolylphosphinic acid,[4]



When the corresponding trichloride is treated with water this acid is produced, and crystallises from dilute alcohol as fine, colourless needles, M.pt. 135° C. The *barium*, *lead*, *copper*, *silver* and *phenylhydrazine salts* are known. Nitration in the usual manner yields *3 : 3′-dinitro-4 : 4′-dimethyldiphenylphosphinic acid*,



forming fine, yellow needles, M.pt. 194° C., readily soluble in alcohol or ether, insoluble in water, and giving a white *silver salt*. Oxidation of di-*p*-tolylphosphinic acid with the requisite amount of alkaline potassium permanganate solution produces *4-methyl-4′-carboxydiphenylphosphinic acid*,



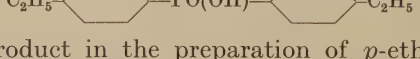
a white crystalline powder, melting above 300° C.

[1] Michaelis and Graeff, *Ber.*, 1875, 8, 1304; Michaelis, *Ber.*, 1877, 10, 627; Michaelis and Link, *Annalen*, 1881, 207, 193.
[2] Schroeder, *Ber.*, 1879, 12, 561.
[3] Dörken, *Ber.*, 1888, 21, 1505.
[4] Michaelis, *Annalen*, 1901, 315, 63.

Di-p-tolylthiophosphinic acid,[1]

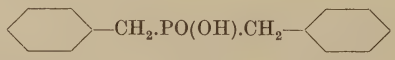
The free acid is unknown, but by heating the corresponding phosphine with water in a sealed tube at 130° to 140° C., a *sulphoxide* results, $[(C_7H_7)_2PS]_2O$. This separates as glistening crystals, M.pt. 165° to 166° C., sparingly soluble in cold alcohol, readily soluble in hot alcohol or ether, sparingly soluble in water, insoluble in sodium or ammonium hydroxide. When heated with water at 180° to 190° C., hydrogen sulphide is evolved and di-*p*-tolylphosphinic acid results. The following derivatives of di-*p*-tolylthiophosphinic acid are known: *amide*, $(C_7H_7)_2PS.NH_2$, a microcrystalline powder, M.pt. 139° C.; *anilide*, $(C_7H_7)_2PS.NHC_6H_5$, fine, matted needles, M.pt. 152° C.; *phenylhydrazide*, $(C_7H_7)_2PS.NH.NHC_6H_5$, fine needles, M.pt. 135·5° C.; *piperidide*, $(C_7H_7)_2PS.NC_5H_{10}$, long needles, M.pt. 134° C.; *diethylamide*, $(C_7H_7)_2PS.N(C_2H_5)_2$, hard compact crystals, M.pt. 177° to 178° C.; *ethyl ester*, $(C_7H_7)_2PS.OC_2H_5$, M.pt. 41° to 42° C.; *phenyl ester*, $(C_7H_7)_2PS.OC_6H_5$, small crystals, M.pt. 135° C.

Di(p-ethylphenyl)phosphinic acid,[2]



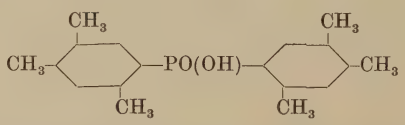
occurs as a by-product in the preparation of *p*-ethylphenyldichlorophosphine by the Friedel-Crafts reaction. It is a pale yellow oil, isolated by decomposing its *copper salt* with concentrated hydrochloric acid.

Dibenzylphosphinic acid,[3]



The formation of this acid has already been described under benzylphosphinic acid, p. 115, the white crystalline mass mentioned in that preparation being extracted with potassium hydroxide and precipitated with hydrochloric acid. From hot alcohol it crystallises in shining scales, M.pt. 191° C., readily soluble in hot nitric acid, not very soluble in the usual solvents. It is only a feeble acid, as it does not turn blue litmus red or liberate carbon dioxide from carbonates. The *potassium* and *silver salts* are known, the latter reacting with methyl iodide to form the *methyl ester*, consisting of bushy, silky prisms, M.pt. 75° C. Nitration produces *4 : 4'-dinitrodibenzylphosphinic acid*, forming colourless needles, M.pt. 225° to 226° C.[4]

Dipseudocumylphosphinic acid,[5]

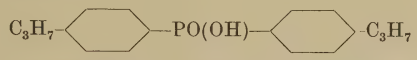


is present in the residues obtained in the preparation of *pseudo*cumyldichlorophosphine, p. 85, and is extracted by petroleum ether. The

[1] Michaelis, *Annalen*, 1901, 315, 66.
[2] Michaelis, *Annalen*, 1896, 293, 220.
[3] Litthauer, *Ber.*, 1889, 22, 2144.
[4] Challenger and Peters, *J. Chem. Soc.*, 1929, p. 2610.
[5] Michaelis, *Annalen*, 1897, 294, 25; Rothe, *Inaug. Dissert. Rostock*, 1892; Uster, *ibid.*, 1896.

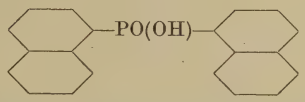
extract is decomposed by water, and the resin obtained is heated under reflux with alcohol and the liquid filtered. The faint yellow filtrate gives crystals which on purification form strongly refractive crystals of the monoclinic system, M.pt. 202° to 203° C., soluble in hot alcohol, acetic acid or boiling benzene, insoluble in water. Bromine in the presence of water decomposes the acid into tribromo*pseudo*cumene and orthophosphoric acid. The following salts are known : *potassium salt* (H_2O), glistening matted needles ; *ammonium salt* ($2H_2O$), white needles ; *barium salt* ($6H_2O$) ; *lead salt*, white precipitate ; *acid* and *neutral silver salts*, white precipitates ; *copper salt* ($10H_2O$), bright blue powder ; *nickel salt* ($10H_2O$), bright green powder ; *cobalt salt*, a dark ultramarine-blue powder. Oxidation of di*pseudo*cumylphosphinic acid (1 mol.) with 4 equivalents of potassium permanganate yields a *di-carboxydimethyldiphenylphosphinic acid*, $(C_8H_8.COOH)_2PO(OH)$, a white, powdery mass, M.pt. 185° C., sparingly soluble in boiling water, readily soluble in alcohol, and giving a *silver salt* as a light, stable powder.

Dicumylphosphinic acid,



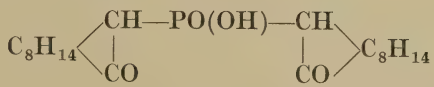
is a white powder, which turns brown on heating and is easily soluble in alcohol or ether, insoluble in water. The *copper salt* is a pale blue powder.

Di-α-naphthylphosphinic acid,[1]



This acid occurs to some extent in the preparation of α-naphthylphosphinic acid (p. 120), and it may also be obtained from the latter by boiling with water. It crystallises in colourless warty groups of needles, M.pt. 202° to 204° C. It liberates carbon dioxide from carbonates and may be precipitated from alkaline solution by the addition of acids.

Dicamphorylphosphinic acid,[2]



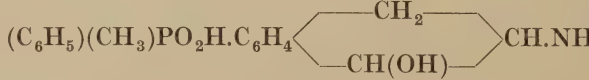
To the sodium camphor obtained by the solution of 75 grams of camphor and 7·5 grams of sodium in 200 c.c. of toluene, 29 grams of phosphorus trichloride diluted with twice its own volume of toluene are slowly added with shaking. Heat is developed and the mass at first partially solidifies, then becoming mobile again, after which it is allowed to stand for one hour. It is then heated gently for thirty minutes and left overnight at room temperature. Water (30 c.c.) is added to the cooled reaction mixture and the aqueous layer separated off. The toluene layer is extracted with 2*N* sodium hydroxide solution, and the cooled alkaline extract acidified with 2*N* hydrochloric acid, when the crude product thus obtained tends to become viscous. Further portions of crude product

[1] Kelbe, *Ber.*, 1878, 11, 1499.
[2] Morgan and Moore, *Trans. Chem. Soc.*, 1910, 97, 1697.

are obtained by evaporation of the first aqueous extract and the filtrate from the precipitated acid, the residue being extracted with alcohol. The acid, which does not crystallise well, deposits colourless nodular crystals from alcohol, decomposing at 283° C., $[\alpha]_D$ 151·1°. It is only sparingly soluble in water, ether or light petroleum, but readily soluble in warm benzene, toluene, chloroform or alcohol. The *sodium*, *lithium*, *silver*, *cadmium*, *copper* and *lead salts* are known.

Phenylmethylphosphinic acid, $(C_6H_5)(CH_3)PO.OH$, may be isolated by treating an aqueous solution of phenyldipiperidylmethylphosphonium iodide with moist silver oxide, the hydroxide obtained being heated for several hours at 150° C.[1] The residue is dissolved in a little water and the silver salt of the acid precipitated by adding a concentrated solution of silver nitrate, the free acid being liberated by hydrochloric acid. A modification of this process [2] consists of heating phenyldipiperidylmethylphosphonium hydroxide at 150° C. for three to four hours, evaporating the residue with ammonium hydroxide on the water-bath until no more ammonia is evolved, then filtering and forming the *silver salt* by the addition of silver nitrate. The silver salt is accurately precipitated by hydrochloric acid, the filtrate from the silver chloride giving the free acid in 75 per cent. yield on evaporation on the water-bath.

The acid forms white needles, M.pt. 133° to 134° C. The *l-menthylamine salt*, $(C_6H_5)(CH_3)PO_2H.C_{10}H_{19}NH_2$, separates as long, colourless, feathery needles, M.pt. 188° to 189° C., very soluble in water or alcohol, less soluble in ethyl acetate, sparingly soluble in acetone; the *cinchonine salt*, $(C_6H_5)(CH_3)PO_2H.C_{19}H_{22}ON_2.2H_2O$, forms small, colourless needles, melting at 170° to 172° C., soluble in alcohol or hot benzene, sparingly soluble in ethyl acetate; the *cinchonidine salt*, $(C_6H_5)(CH_3)PO_2H.C_{19}H_{22}ON_2.4H_2O$, yields beautiful colourless prisms, M.pt. 154° C., very soluble in alcohol, benzene or boiling water, sparingly soluble in ethyl acetate or cold water; the *quinine salt*, $(C_6H_5)(CH_3)PO_2H.C_{20}H_{24}O_2N_2.4H_2O$, begins to melt at 85° C., the anhydrous salt melting at 164° to 166° C., and is readily soluble in alcohol, hot ethyl acetate or water, sparingly soluble in cold water; the *hydroxyhydrindamine salt*,



forms light silky needles, decomposing at about 170° C. without melting, and readily soluble in alcohol, sparingly soluble in ethyl acetate or acetone; the *l-hydroxyhydrindamine salt* decomposes at 175° C. and has similar properties to the foregoing salt.

Phenylmethylphosphinic acid (15 grams) combines with thionyl chloride (25 c.c.) when heated with it under reflux for thirty minutes on the water-bath; a 94 per cent. yield of *phenylmethylphosphinyl chloride*, $C_6H_5(CH_3)POCl$, results.[3] The product is a colourless liquid, B.pt. 155° C. at 11 mm. or 167° C. at 22 mm., fuming in air and having an odour reminiscent of thiocarbonyl chloride. It reacts vigorously with water, yielding phenylmethylphosphinic acid. It combines with

[1] Michaelis, *Annalen*, 1896, 293, 220.
[2] Pope and Gibson, *Trans. Chem. Soc.*, 1912, 101, 740.
[3] Gibson and Johnson, *J. Chem. Soc.*, 1928, p. 92.

aniline, giving *phenylmethylphosphinanilide*, colourless needles, M.pt. 142° C., and with absolute alcohol to give *ethyl phenylmethylphosphinate*, $C_6H_5(CH_3)PO.OC_2H_5$, a colourless, highly refractive liquid, B.pt. 143° C. at 11 mm., the parachor [*P*] being 417·3 (for semipolar double bond) and 442·1 (for non-polar double bond). The *methyl ester* boils at 137° C. at 11 mm.

Phenylisobutylphosphinic acid,[1] $(C_6H_5)(C_4H_9)PO.OH$, occurs when *iso*butyl iodide reacts with di-*iso*butyl phenylphosphinite at 160° C. in a sealed tube. It melts at 64° to 65° C., but its salts with the alkali metals or alkaloids are not crystalline.

Phenyltriphenylmethylphosphinic acid, $(C_6H_5)[(C_6H_5)_3C]PO.OH$, is obtained when the *iso*butyl iodide in the foregoing reaction is replaced by triphenylmethyl bromide. It melts at 287° to 288° C., but does not yield crystalline salts.

Phenylhydroxyethylphosphinic acid, $(C_6H_5)[CH(OH)CH_3]PO.OH$.[2]—One molecular proportion of phenyldichlorophosphine is allowed to react with acetaldehyde (1 mol.), the mixture being cooled in ice. After completion of the reaction the mixture is poured into a large bulk of water and evaporated down with frequent additions of water. An oil results which crystallises in stellate groups of needles, M.pt. 104° C., soluble in water but insoluble in ether. The *barium salt* contains four molecules of water of crystallisation and separates in needles. Propyl aldehyde and *iso*butyl aldehyde are said to react in a similar manner to acetaldehyde, but the products are non-crystallisable oils.

Phenylhydroxybenzylphosphinic acid, $(C_6H_5)[CH(OH)C_6H_5]PO.OH$, occurs when the acetaldehyde in the foregoing reaction is replaced by benzaldehyde. It is a white, granular powder, M.pt. 112° to 114° C., and its *barium salt* (H_2O) crystallises in plates.

Phenyltolylphosphinic acid, $(C_6H_5)(C_7H_7)PO.OH$, crystallises in fine needles, M.pt. 116° C., yielding on nitration with fuming nitric acid a *dinitrophenyltolylphosphinic acid*, $(C_6H_4.NO_2)(C_7H_6.NO_2)PO.OH$, consisting of small yellow needles, M.pt. 205° C., which explode on direct heating.

Phenylpseudocumylphosphinic acid, $(C_6H_5)(C_9H_{11})PO.OH$, forms needles, M.pt. 181° C. It yields a *phenylhydrazine salt*, white needles, M.pt. 140·5° C., and a *trinitro-derivative*, yellow prisms, M.pt. 197° to 198° C.

p-Tolylmethylphosphinic acid, $(CH_3.C_6H_4)(CH_3)PO.OH$,[3] occurs when methyl-*p*-tolyldipiperidine-N-phosphonium iodide is heated at 180° C. It forms white needles, M.pt. 120° C., readily soluble in alcohol, sparingly soluble in water, and gives a *silver salt*, crystallising in pearly plates.

Tolylbenzylphosphinic acid, $(C_7H_7)(C_6H_5.CH_2)PO.OH$, is isomeric with ditolylphosphinic acid.[4] When tritolylphosphine and benzyl chloride are heated together for five to seven hours at 170° C., an oily phosphonium compound results. The latter yields a *diphenoxy-derivative* when shaken with cold dilute sodium hydroxide solution, and subsequent treatment with water gives the *phenyl ester* of the acid :

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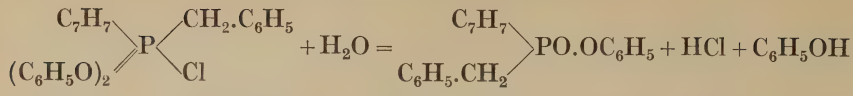
[1] Arbusoff and Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 1905.
[2] Holle, *Inaug. Dissert. Rostock*, 1892.
[3] Michaelis, *Ber.*, 1898, 31, 1037.
[4] Michaelis, *Annalen*, 1901, 315, 70.



This ester separates from aqueous alcohol as small, white crystals, M.pt. 120° C., soluble in benzene or petroleum ether. It is converted into the acid by heating under reflux for several hours with concentrated alcoholic potassium hydroxide. The acid crystallises from alcohol as white, glistening needles, M.pt. 145° C., soluble in ether or benzene. The *silver salt* is a pure white crystalline powder, becoming dark on exposure to light.

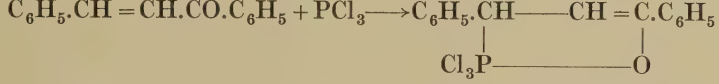
CHAPTER III.

MISCELLANEOUS PHOSPHORUS COMPOUNDS.

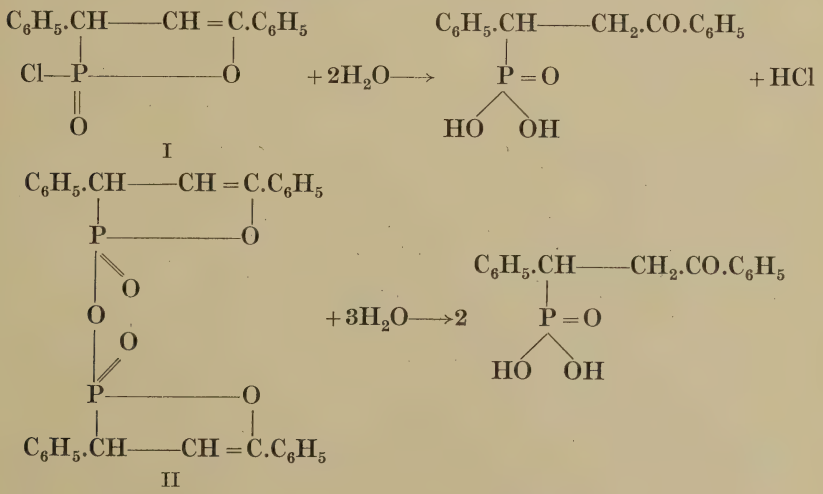
Compounds derived from Aldehydes and Ketones.

The Reaction between Phosphorus Trichloride and Unsaturated Ketones.

When phosphorus trichloride is condensed with $\alpha\beta$-unsaturated ketones in glacial acetic acid solution and the mixture is diluted with water, β-ketophosphinic acids are obtained.[1] On replacing the acetic acid by acetic anhydride it has been shown that the addition takes place at the 1 : 4-position, as follows : [2]



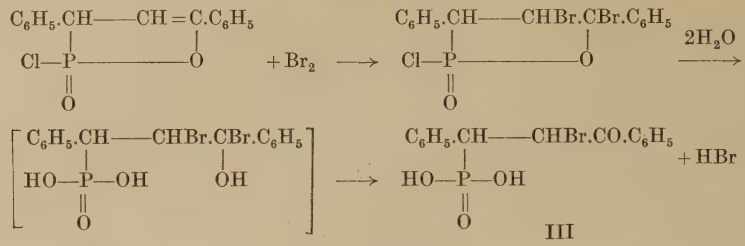
Phosphorus trichloride, benzal acetophenone (phenyl styryl ketone) and acetic anhydride react at room temperature forming acetyl chloride and a compound which yields a ketophosphinic acid with water. The intermediate product is a thick oil, supposed to be a mixture of the acid chloride I and the acid anhydride II, both of which are decomposed by water to form the phosphinic acid :



Product I is formed if 1 molecular equivalent of acetic anhydride is used ; excess of the anhydride leads to the production of varying amounts of product II. Both the compounds are unsaturated, and the position of the double bond is ascertained by treating the substances

[1] Conant, *J. Amer. Chem. Soc.*, 1917, 39, 2679. [2] Conant and Cook, *ibid.*, 1920, 42, 830.

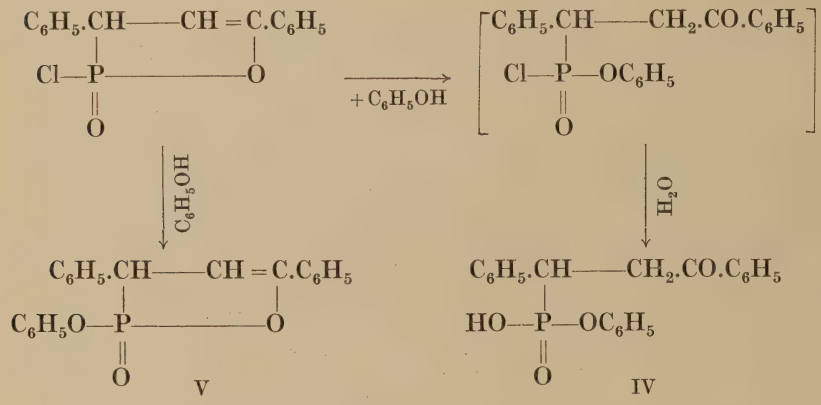
with bromine and acting upon the dibromide with water, when decomposition takes place and a β-bromoketophosphinic acid (III) and hydrogen bromide are formed. Thus, in the case of I :



III

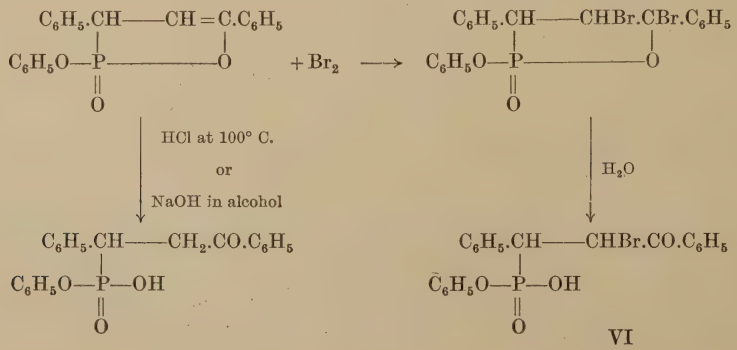
If the anhydride II is used, the reactions are essentially the same as those indicated in the foregoing scheme.

The compound I gives rise to two substances when treated with phenol, a monophenyl ester (IV), and a phenyl ester of an unsaturated cyclic acid (V) :



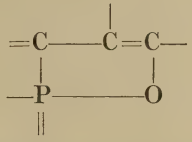
V IV

The ester V combines with bromine and is therefore unsaturated ; it may also be converted by acids or bases into the monophenyl ester of the ketophosphinic acid. The ring is more stable in the case of the ester than the acid chloride, and the position of the double bond may be shown by transforming the bromine addition product into a monophenyl ester of the β-bromoketophosphinic acid (VI) :



VI

The foregoing schemes prove that the intermediate product formed when acetic anhydride is used consists of a mixture of two unsaturated cyclic compounds, both containing the linkage



β-Benzoyl-α-4-methoxyphenylethylphosphinic acid, $CH_3O.C_6H_4.CH[PO(OH)_2].CH_2.CO.C_6H_5$.—19 grams of phenyl *p*-methoxystyryl ketone (anisal acetophenone) are partly dissolved in 40 c.c. of glacial acetic acid and 14 grams of phosphorus trichloride added. The ketone dissolves and the solution becomes red. After standing overnight the mixture is poured into 500 c.c. of water, an oil separating out and solidifying on stirring. The product is dissolved in aqueous sodium carbonate solution and extracted with ether, the latter removing a small quantity of yellow material. Acidification of the solution gives an 89 per cent. yield of the phosphinic acid. The acid forms small, colourless needles, M.pt. 189° C., soluble in alcohol, sparingly soluble in boiling water, practically insoluble in cold water or ether. It yields an *oxime*, which is a crystalline solid, melting with slight decomposition at 156° C. The acid does not react with bromine in cold chloroform solution and cannot be hydrolysed by 50 per cent. sodium hydroxide or heating with concentrated hydrochloric acid. It forms a crystalline *sodium salt*, soluble *calcium* and *barium salts*, and insoluble *silver* and *lead salts*.

β-Benzoyl-α-phenylethylphosphinic acid, $C_6H_5.CH[PO(OH)_2].CH_2.CO.C_6H_5$.—This acid occurs when the phenyl *p*-methoxystyryl ketone in the preceding preparation is replaced by phenyl styryl ketone (benzal acetophenone). The product contains 0·75 molecule of water of crystallisation, which is lost at 116° C. when the compound melts.

β-Cinnamoyl-α-phenylethylphosphinic acid,

$$C_6H_5.CH[PO(OH)_2].CH_2.CO.CH=CH.C_6H_5$$

occurs when distyryl ketone (dibenzal acetone) is used in the reaction. It contains 1·25 molecules of water of crystallisation, which it loses at 108° C. It reduces potassium permanganate solution and combines with bromine in cold chloroform.

β-Bromo-β-benzoyl-α-phenylethylphosphinic acid, $C_6H_5.CH[PO(OH)_2].CHBr.CO.C_6H_5$, may be obtained by brominating β-benzoyl-α-phenylethylphosphinic acid or by bromination as shown on p. 128 (compound III). It is a white, crystalline solid, M.pt. 196° C., converted by sodium carbonate, bicarbonate or hydroxide into phenyl styryl ketone, sodium bromide and sodium phosphate. When a boiling chloroform solution of the bromo-acid is treated with 1 equivalent of thionyl chloride, it yields the *acid chloride*, which with phenol gives the *monophenyl ester*, a crystalline product, M.pt. 179° C. The ester is best obtained by brominating phenyl β-benzoyl-α-phenylethylphosphinate described overpage; it forms a *sodium salt* with cold dilute sodium hydroxide, but if the reaction be carried out with

warming, decomposition takes place with formation of phenyl styryl ketone.

Phenyl β-benzoyl-α-phenylethylphosphinate, $C_6H_5.CO.CH_2.CH.C_6H_5.[PO(OH)]OC_6H_5$.—The phosphinic acid is treated with 1 equivalent of thionyl chloride and the resulting acid chloride heated with phenol. The ester is a crystalline product, M.pt. 146° C.

Diphenyl β-benzoyl-α-phenylethylphosphinate results in small amount during the preceding reaction, but is obtained in better yield by using 2 equivalents of thionyl chloride and 2 equivalents of phenol. It may be crystallised from alcohol, and melts at 125° C. It is readily hydrolysed to the *monophenyl ester* by cold sodium ethylate, and both esters are hydrolysed to the free acid by warming with aqueous sodium hydroxide.

The Mechanism of the Reaction of Phosphorus Trichloride with Benzaldehyde.[1]

Whereas in the preceding section the phosphorus addition took place at the 1 : 4-position, the addition here is at the 1 : 2-position, as follows :—

$$C_6H_5.CHO + PCl_3 \rightleftharpoons C_6H_5.CH\begin{cases}O\\ |\\ PCl_3\end{cases}$$

Only about 30 per cent. of the addition product is formed, the reaction being reversible and the factors governing the equilibrium being capable of expression in terms of the law of mass action. The values obtained for the equilibrium constant vary from 6·9 to 8·3, the average being 7·4. The product is converted by water into the corresponding phosphinic acid :

$$C_6H_5.CH\begin{cases}O\\ |\\ PCl_3\end{cases} + 3H_2O = C_6H_5.\underset{\displaystyle PO(OH)_2}{\underset{|}{CHOH}} + 3HCl$$

The addition product reacts with acetic anhydride to form acetyl chloride and a mixture of an acid chloride (I) and an acid anhydride (II), a large excess of acetic anhydride converting most of (I) into (II) :

$$C_6H_5.CH\begin{cases}O\\ |\\ PCl_3\end{cases} + (CH_3.CO)_2O = \underset{\text{I}}{C_6H_5.CH\begin{cases}O\\ |\\ POCl\end{cases}} + 2CH_3COCl$$

$$2C_6H_5.CH\begin{cases}O\\ |\\ PCl_3\end{cases} + (CH_3.CO)_2O \longrightarrow \underset{\text{II}}{\left(C_6H_5.CH\begin{cases}O\\ |\\ PO\end{cases}\right)_2 O} + 2CH_3COCl$$

The mixture of acid chloride and anhydride remains as a gum after removing the acetyl chloride and excess of acetic anhydride. This gum when treated with water yields hydrogen chloride and a monobasic acid containing a three-membered carbon-oxygen-phosphorus ring, and the name "*phostonic*" *acids* is suggested for acids of this type :

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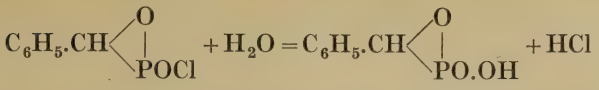
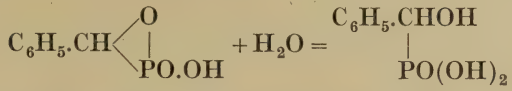
[1] Conant and MacDonald, *J. Amer. Chem. Soc.*, 1920, 42, 2337; compare Page, *Trans. Chem. Soc.*, 1912, 101, 423.

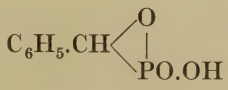


The amount of chlorion thus produced is obviously a measure of the amount of acid chloride present in the mixture. The acid is isolated in the form of an insoluble barium salt, the structure of which follows from the fact that the acid is monobasic and on boiling with water is converted into the hydroxyphosphinic acid :



The cyclic acid reduces potassium permanganate slowly, whereas the hydroxy-acid is oxidised immediately by this reagent. The three-membered ring is much more stable than the corresponding five-membered ring (p. 127) obtained with the unsaturated ketones ; this fact may be due to the presence of the ethylene linkage in the latter ring.

Anhydro-α-hydroxybenzylphosphinic acid,

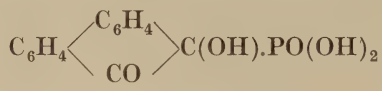


10 grams of benzaldehyde, 13 grams of phosphorus trichloride and 20 grams of acetic anhydride are mixed in a 150 c.c. distilling flask fitted with a calcium chloride tube, the temperature being kept below 40° C. After standing overnight at room temperature, the contents of the flask are evaporated at 50° C. and 50 to 60 mm. for 2 hours. A viscous residue weighing 22 grams results, but although soluble in chloroform, it cannot be crystallised from that solvent. This gum with barium hydroxide forms the *barium salt* of the required acid, and the salt on acidification gives the free acid, which is ground with water, spread on a tile and dried over sulphuric acid. The acid is purified by dissolving in alcohol and evaporating down, but about 10 per cent. of barium always remains in the product. The acid decolorises permanganate solution only one-seventh as fast as a hydroxyphosphinic acid. It does not form a crystalline aniline salt when its ether solution is treated with aniline. If 2 grams of the acid be warmed on a steam-bath with 75 c.c. of concentrated hydrochloric acid until a clear solution results, filtration and addition of dilute sulphuric acid precipitates the barium, and the filtered solution when evaporated to dryness yields the crude α-hydroxybenzylphosphinic acid.

α-Hydroxybenzylphosphinic acid, $C_6H_5.CH(OH)PO(OH)_2$, may be obtained as just described, or as follows : 10 grams of benzaldehyde and 14 grams of phosphorus trichloride are cautiously mixed in a flask fitted with a calcium chloride guard tube. After one hour 18 grams of glacial acetic acid are added and the mixture allowed to stand for three hours. The temperature should be maintained at 25° to 35° C. during the entire preparation. The mixture is then poured into 200 c.c. of water and the liquor evaporated to dryness on the steam-bath. The residue is dissolved in a little alcohol and the solution

diluted with 100 c.c. of ether. 10 grams of aniline in 10 c.c. of ether are added and the *aniline salt* of the acid filtered off. The yield is about 18 grams, or 72 per cent. The aniline salt may be recrystallised from alcohol; it melts with decomposition at 201° to 202° C. The free acid, isolated from the salt in the usual manner, melts at 170° to 172° C.[1] The acid yields *normal* and *acid barium salts.*

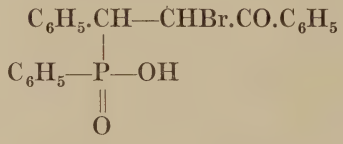
α-Hydroxyphenanthraquinonephosphinic acid,[2]



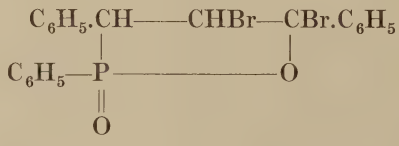
occurs when phenanthraquinone is digested with phosphorus trichloride. It forms flesh-coloured flakes, which appear crystalline under the microscope and melt at 125° to 128° C. It readily dissolves in water, alcohol, ether or glacial acetic acid, forming a deep red solution in the latter. Oxidation by permanganate in acid solution yields phenanthraquinone and phosphoric acid. The *calcium salt* separates as deep green flocks when calcium chloride is added to an aqueous solution of the acid.

The 1 : 4 Addition of Phenyldichlorophosphine.[3]

The addition of phenyldichlorophosphine to phenyl styryl ketone (benzal acetophenone) in acetic acid solution yields exactly the same types of compounds as are obtained by the use of phosphorus trichloride (p. 127). The structure of the various compounds is proved as before by resorting to bromination. The product



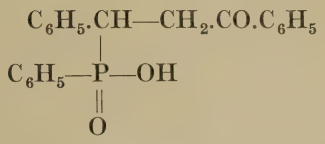
contains two asymmetric carbon atoms, so that two racemic stereoisomers are possible; both may be formed by brominating the ketophosphinic acid or by the action of water on the cyclic dibromide



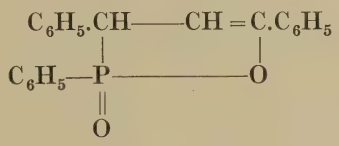
These two isomeric bromine compounds are stereoisomers and not structural isomers, since they are both decomposed by alkaline reagents with the formation of benzal acetophenone. The lower-melting isomer may be transformed into the higher-melting one by the prolonged action of sunlight on its chloroform solution.

[1] Compare Fossek, *Monatsh.*, 1886, 7, 20.
[2] Fossek, *ibid.*
[3] Conant and Pollack, *J. Amer. Chem. Soc.*, 1921, 43, 1665.

Phenyl-β-benzoyl-α-phenylethylphosphinic acid,

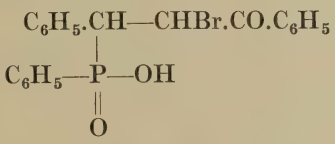


9 grams of phenyldichlorophosphine in 15 grams of glacial acetic acid are treated with 10 grams of phenyl styryl ketone (benzal acetophenone), the mixture being cooled in water during the addition. When no more solid separates, 70 c.c. of glacial acetic acid are stirred in, and after 30 minutes the mixture is poured into water. The solid is filtered off, washed with alcohol and dried, about 19 grams of crude product being isolated. This is purified by solution in aqueous sodium carbonate, extraction with ether and precipitation from the aqueous layer by the addition of acid. The product is practically insoluble in all solvents, but may be recrystallised from its very dilute solution in hot glacial acetic acid or ethyl alcohol, the resulting substance melting at 220° to 225° C. with decomposition. Replacing the acetic acid in the foregoing reaction by acetic anhydride, the unsaturated cyclic anhydride



is isolated in the impure state as a gum which readily reacts with water to give the ketophosphinic acid. With *bromine* the anhydride forms an *addition product*, which reacts with water to give the two stereoisomeric acids described below.

Phenyl-β-bromo-β-benzoyl-α-phenylethylphosphinic acid,

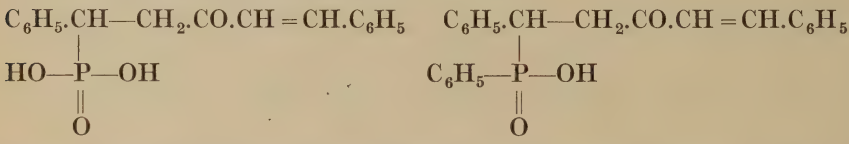


5 grams of phenyl-β-benzoyl-α-phenylethylphosphinic acid are suspended in 20 c.c. of glacial acetic acid and the mixture raised to the boiling-point, when a small amount of bromine is added and the heating continued until all the colour disappears (after about 5 minutes). More bromine is then slowly added, the mixture being kept just off the boil; hydrogen bromide is evolved and the solid matter gradually disappears. At the completion of the reaction the clear solution is poured into 500 c.c. of water and the precipitated solid filtered off and dried. The yield is about 6·5 grams of product of M.pt. 160° to 180° C. Another method of preparation is by bromination of the cyclic anhydride followed by treatment with water, as mentioned already. The *two isomers* are obtained from the crude product by treating it with 50 c.c. of hot chloroform, filtering and evaporating to 20 c.c., then adding petroleum ether, when the lower-melting isomer slowly crystallises. Two grams separate, M.pt. 160° to 180° C. The

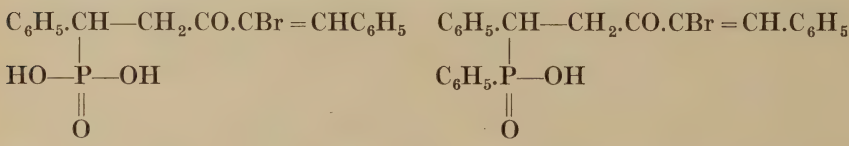
insoluble portion, recrystallised from ethyl alcohol, yields one gram of the higher-melting isomer, M.pt. 195° C. Both isomers dissolve in aqueous sodium carbonate and both are decomposed by sodium hydroxide, yielding phenyl styryl ketone. If a chloroform solution of the lower-melting isomer, containing a trace of iodine, be exposed to sunlight, the higher-melting isomer separates, but many weeks elapse before half the lower-melting body is transformed to the higher-melting one.

The Interaction of Phosphorus Halides with Distyryl Ketone and Phenyl Cinnamylidene Methyl Ketone.[1]

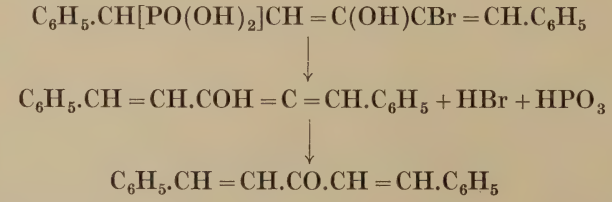
Phosphorus trichloride and phenyldichlorophosphine react with distyryl ketone (dibenzal acetone) in acetic acid solution giving respectively β-cinnamoyl-α-phenylethylphosphinic acid and phenyl-α-phenyl-β-cinnamoylethylphosphinic acid:



Both compounds combine with two atoms of bromine, and are readily oxidised with formation of benzaldehyde. The second, when oxidised by ozone, gives a dibasic acid of the formula $C_6H_5.CH[C_6H_5.PO(OH)]CH_2.COOH$. The dibromides readily evolve hydrogen bromide with alkaline reagents and form unsaturated monobromo-acids :



These unsaturated bromo-acids are soluble without decomposition in sodium carbonate solution, but aqueous potassium hydroxide decomposes them, forming benzaldehyde and removing the bromine and phosphorus radicals. The first bromo-acid also gives a small yield of dibenzal acetone, the use of alcoholic potassium hydroxide increasing the yield of unsaturated ketone to 25 per cent. ; the reaction taking place is probably as follows :



The interaction of phosphorus trichloride and cinnamylidene acetophenone is unsatisfactory and only a small yield of ketophosphinic acid results, but phenyldichlorophosphine gives a fair yield of phenyl-

[1] Conant, Bump and Holt, *J. Amer. Chem. Soc.*, 1921, **43**, 1677.

β-benzoyl-α-styrylethylphosphinic acid, which yields benzaldehyde on oxidation with ozone, showing that the addition takes place in the 1 : 4 and not the 1 : 6-position :

$$C_6H_5.CH=CH.CH=CH.CO.C_6H_5 + C_6H_5PCl_2 + 2CH_3COOH \rightarrow$$

$$C_6H_5.CH=CH.\underset{\displaystyle C_6H_5\text{—}\underset{\displaystyle \underset{\displaystyle O}{\|}}{P}\text{—}OH}{\underset{|}{CH}}.CH_2.CO.C_6H_5 + 2CH_3COCl$$

Phenyl-α-phenyl-β-cinnamoylethylphosphinic acid, $C_6H_5.CH(C_6H_5.PO.OH).CH_2.CO.CH=CH.C_6H_5$.—Dibenzal acetone is suspended in acetic acid and treated with phenyldichlorophosphine. The resulting solid is dissolved in 20 per cent. aqueous sodium hydroxide and the solution extracted with ether to remove unchanged ketone, addition of hydrochloric acid then precipitating the acid. Filtration and recrystallisation from hot glacial acetic acid gives a 53 per cent. yield of the phosphinic acid. The acid melts at 235° to 236° C., and is practically insoluble in all the common solvents. When a chloroform solution of the acid is oxidised by dry ozone and subsequently evaporated under diminished pressure at 40° C., benzaldehyde results. If the aldehyde be removed in steam, a gummy mass remains and the aqueous solution on evaporation yields a grey crystalline solid. This is *phenyl-α-phenyl-β-carboxyethylphosphinic acid,* $C_6H_5.CH(C_6H_5.PO.OH)CH_2.COOH$, M.pt. 212° C., which may be recrystallised from hot water. Titration with sodium hydroxide shows it to be dibasic.

α-Phenyl-$\beta(\alpha'\beta'$-dibromo-β'-phenylpropionyl)-ethylphosphinic acid or **α-Phenyl-β(dibromohydrocinnamoyl)-ethylphosphinic acid,** $C_6H_5.CH[PO(OH)_2].CH_2.CO.CHBr.CHBr.C_6H_5$, is formed by brominating the corresponding unsaturated acid, the reaction being accelerated by sunlight. It crystallises from moist chloroform or aqueous alcohol as fine, white needles, M.pt. 180° to 182° C. with decomposition. The crystals contain 2·5 molecules of water.

α-Phenyl-$\beta(\alpha'$-bromocinnamoyl)-ethylphosphinic acid, $C_6H_5.CH[PO(OH)_2].CH_2.CO.CBr=CH.C_6H_5$, results on acting upon the foregoing crystalline dibromide with alcoholic potash. The yield is about 81 per cent. and the product crystallises from aqueous alcohol in fine needles, containing some water of crystallisation which is lost when the compound melts at 130° to 132° C. The acid readily dissolves in sodium bicarbonate without decomposition, reduces alkaline permanganate solution instantly, but does not combine with bromine. Oxidation by ozone gives benzoic acid, no benzaldehyde being produced. From the ozonised solution *α-phenyl-β-glyoxyethylphosphinic acid* separates. This melts with decomposition at 183° C., is tribasic, and when heated loses carbon dioxide and water, forming α-phenyl-β-carboxyethylphosphinic acid, $C_6H_5.CH[PO(OH)_2].CH_2.COOH$.

Phenyl-α-phenyl-$\beta(\alpha'\beta'$-dibromophenylpropionyl)-ethylphosphinic acid results when the corresponding unsaturated monobasic acid is brominated. The yield is quantitative and the bromo-acid separates from hot glacial acetic acid in crystals, M.pt. 195° C. with decomposition. It slowly dissolves in cold sodium carbonate or bicarbonate

solution, from which it may be precipitated unchanged. Solution in a hot 4 per cent. solution of potassium acetate in methyl alcohol and heating for a few minutes on the water-bath gives, on pouring into water, an 80 per cent. yield of *phenyl-α-phenyl-β(α′-bromocinnamoyl)-ethylphosphinic acid*, M.pt. 200° C. Alcoholic potassium hydroxide transforms this into dibenzal acetone.

β-Benzoyl-α-styrylethylphosphinic acid, $C_6H_5.CH=CH.CH[PO(OH)_2].CH_2.CO.C_6H_5$.—This is prepared by condensing phosphorus trichloride and phenyl cinnamylidenemethyl ketone in acetic anhydride solution and subsequently treating the mixture with water. The acid contains 0·25 molecule of water, and melts at 159° to 161° C.

Phenyl - β - benzoyl - α - styrylethylphosphinic acid, $C_6H_5.CH=CH.CH(C_6H_5.PO.OH).CH_2.CO.C_6H_5$, occurs in 64 per cent. yield when phenyldichlorophosphine and phenyl cinnamylidenemethyl ketone are condensed in glacial acetic acid and the solution treated with water. When recrystallised from hot glacial acetic acid it melts at 200° C. and is insoluble in most solvents.

The Action of Phosphorus Trichloride on Saturated Aldehydes and Ketones.[1]

It has already been shown that phosphorus trichloride reacts with benzaldehyde in acetic acid solution to yield α-hydroxybenzylphosphinic acid, and this process is here extended. The phosphorus trichloride is added to the carbonyl compound below 35° C., or sometimes cooling is necessary, and at least a 10 per cent. excess of trichloride is used. The mixture is protected from moisture and allowed to stand for two to three hours. A slight excess (3 molecular equivalents) of glacial acetic acid is then added, the mixture being kept between 20° and 30° C. After 12 hours the liquid is poured into 300 c.c. of ice-water and shaken vigorously. Evaporation of the solution yields a gum, which may take from one day to three weeks to crystallise. The crystalline mass is dried on a plate and finally in a desiccator over sodium hydroxide. If no crystalline product can be isolated, the lead salt is prepared as follows : The gum is dissolved in about 200 c.c. of water, the solution made strongly alkaline with ammonium hydroxide, then treated with magnesium nitrate. After standing overnight, the precipitated magnesium ammonium phosphate is filtered off, the solution diluted to 500 c.c., just acidified with acetic acid and heated to boiling. An excess of lead acetate or nitrate solution is then added, the whole boiled for 5 to 10 minutes and then filtered. The lead salt is washed with boiling water and dried, the product being free from phosphate and practically free from chloride.

α-Phenylvinylphosphinic acid, $CH_2=CC_6H_5.PO(OH)_2$, occurs when acetophenone is used. It is a solid, M.pt. 112° C., very soluble in water, fairly soluble in alcohol, sparingly soluble in benzene and best recrystallised from benzene-carbon tetrachloride mixture. The *aniline salt* melts at 180° to 181° C. The acid decolorises bromine water immediately and bleaches potassium permanganate solution. Oxidation by chromic acid yields formaldehyde as one of the products.

α-Hydroxyisopropylphosphinic acid is formed in 91 per cent.

[1] Conant, MacDonald and Kinney, *J. Amer. Chem. Soc.*, 1921, 43, 1928.

yield when acetone is used in the reaction. The product melts at 167° to 169° C.[1]

α-Hydroxy-α-methylpropylphosphinic acid, obtained from methyl ethyl ketone, is isolated only in the form of its *lead salt*, $C_2H_5.C(PO_3Pb)OH.CH_3$, which is insoluble in water but fairly soluble in concentrated nitric acid. If ethyl propyl ketone be used, the *lead salt* of *α-hydroxy-α-ethylbutylphosphinic acid* is produced, $C_3H_7.C(PO_3Pb)OH.C_2H_5$, and with pinacoline the *lead salt* of *α-hydroxy-αββ-trimethylpropylphosphinic acid*, $(CH_3)_3C-C(PO_3Pb)OH.CH_3$, results, which is a very hygroscopic substance.

α-Hydroxy-β-phenyl-α-benzylethylphosphinic acid, $C_6H_5.CH_2.[PO(OH)_2]COH.CH_2.C_6H_5$, is the reaction product when dibenzyl ketone is used. The acid may be recrystallised from benzene and melts at 181° to 182° C. Benzylacetophenone yields *α-phenyl-α-hydroxy-γ-phenylpropylphosphinic acid*, $C_6H_5.C[PO(OH)_2]OH.CH_2.CH_2.C_6H_5$, of M.pt. 165° to 168° C., practically insoluble in water, soluble in alcohol, ether or acetic acid, and unaffected by bromine water. Dibenzyl acetone forms *α-hydroxy-α(β-phenylethyl)-γ-phenylpropylphosphinic acid*, $(C_6H_5.CH_2.CH_2)_2C(OH)[PO(OH)_2]$, M.pt. 173° to 174° C., insoluble in water but soluble in sodium bicarbonate solution.

Benzil, camphor, benzophenone and anthraquinone do not react under the foregoing conditions using acetic acid or acetic anhydride. Benzil and anthraquinone do not react under any conditions, and camphor does not give any amount of crystalline product.

α-Hydroxydiphenylmethylphosphinic acid, $(C_6H_5)_2C(OH)[PO(OH)_2]$.—Benzophenone is melted on the steam-bath with benzoic acid and phosphorus trichloride added in small portions, the temperature being raised to 155° C. during the course of ten minutes, then allowed to fall to 130° C. and so maintained for two to three hours. The mixture is then cooled to 90° C., poured into 500 c.c. of water, made strongly alkaline with sodium hydroxide and heated on the steam-bath for four to five hours. The whole is then diluted to 750 c.c. and unchanged benzophenone extracted with ether. To separate the benzoic acid the mixture is strongly acidified with hydrochloric acid, cooled and filtered. The filtrate is evaporated to 250 c.c. and extracted three times with ether. The ether filtrate on evaporation yields an oil which solidifies. Recrystallised from feebly acidified water the acid melts at 171° to 172° C.

It has been shown that acetophenone, phosphorus trichloride and glacial acetic acid react as follows :

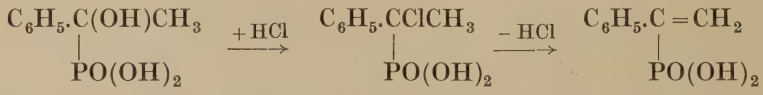
$$C_6H_5.CO.CH_3 + PCl_3 + CH_3COOH \longrightarrow 2CH_3COCl + HCl + C_6H_5.C(O)(PO.OH)-CH_3$$

The phosphinic acid on treatment with water reacts according to the equation

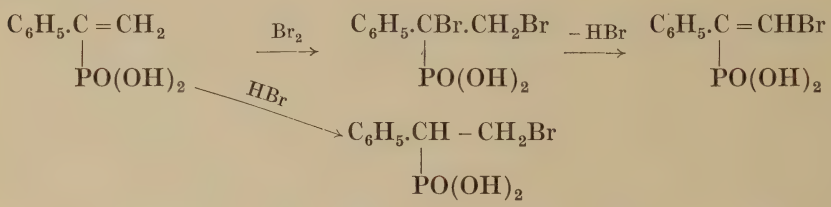
$$C_6H_5.C(O)(PO.OH)-CH_3 + H_2O = C_6H_5.C(OH)(PO(OH)_2)CH_3$$

[1] Compare Marie, *Compt. rend.*, 1901, 133, 221.

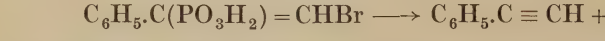
If acetophenone, phosphorus trichloride and glacial acetic acid are mixed and the mixture saturated the next day with hydrogen chloride, α-chloro-α-phenylethylphosphinic acid results.[1] Loss of hydrogen chloride by the chloro-acid then gives an unsaturated acid :



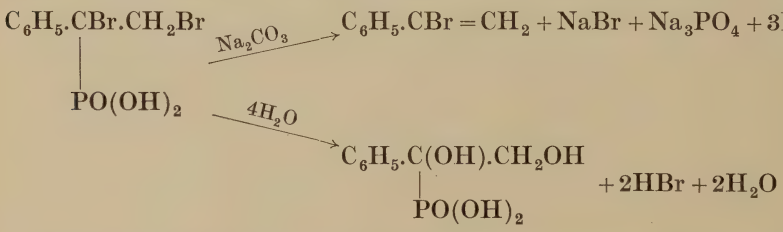
Bromination of the unsaturated acid yields a dibromo-acid which loses hydrogen bromide above its melting-point, forming an unsaturated bromo-acid :



Sodium carbonate converts the unsaturated bromo-acid into phenylacetylene :



The dibromo-acid yields a dihydroxy-acid when treated with water alone, but with aqueous sodium carbonate it gives α-bromostyrene :



The compounds prepared according to the foregoing scheme are as follows :—

α-Chloro-α-phenylethylphosphinic acid.—This acid melts at 174° to 175° C. When heated above its melting-point or when boiled in aqueous solution it is converted into α-phenylvinylphosphinic acid. This acid on bromination forms *αβ-dibromo-α-phenylethylphosphinic acid*, M.pt. 186° to 188° C., which evolves hydrogen bromide above its melting-point and forms *β-bromo-α-phenylvinylphosphinic acid*, M.pt. 133° to 135° C. These two bromo-acids with aqueous sodium carbonate yield α-bromostyrene and phenylacetylene respectively, as indicated by the foregoing schemes. The dibromo-acid is converted by water into *αβ-dihydroxy-α-phenylethylphosphinic acid*, M.pt. 143° to 145° C. *β-Bromo-α-phenylethylphosphinic acid* occurs when α-phenylvinylphosphinic acid is heated with hydrobromic acid for 17 hours in a sealed tube at 100° C.; chlorine converts the unsaturated acid into *αβ-dichloro-α-phenylethylphosphinic acid*, M.pt. 175° to 178° C.

[1] Conant and Coyne, *J. Amer. Chem. Soc.*, 1922, 44, 2530.

The Interaction of Diphenylchlorophosphine with Benzaldehyde and Benzalacetophenone.[1]

Diphenylchlorophosphine reacts with benzaldehyde and with benzalacetophenone (phenyl styryl ketone) in the presence of glacial acetic acid according to the schemes :

$$C_6H_5.CHO + (C_6H_5)_2PCl + CH_3COOH = C_6H_5.CHOH.PO(C_6H_5)_2 + CH_3COCl$$

$$C_6H_5.CH=CH.CO.C_6H_5 + (C_6H_5)_2PCl + CH_3COOH \longrightarrow C_6H_5.\underset{\displaystyle (C_6H_5)_2P(=O)}{\underset{|}{CH}}.CH_2.C_6H_5 + CH_3COCl$$

I

If the acetic acid be replaced by acetic anhydride the reaction takes the following course, an unsaturated ketone resulting, which may undergo reactions as shown :

$$C_6H_5.CH=CH.CO.C_6H_5 + (C_6H_5)_2PCl + (CH_3CO)_2O$$

$$\downarrow$$

$$O{-}(C_6H_5)_2P{-}O{-}P(C_6H_5)_2{-}O$$
$$|\quad\quad|\quad\quad|\quad\quad|$$
$$C=CH{-}{-}CH\quad CH{-}CH=C$$
$$|\quad\quad|\quad\quad|\quad\quad|$$
$$C_6H_5\quad C_6H_5\quad C_6H_5\quad C_6H_5$$

II

$\xrightarrow{H_2O}$

$$C_6H_5$$
$$|$$
$$CH{-}CH_2.CO.C_6H_5$$
$$|$$
$$O=P(C_6H_5)_2$$

$\downarrow Br_2$

$$O{-}{-}{-}(C_6H_5)_2P{-}O{-}P(C_6H_5)_2{-}{-}{-}O$$
$$|\quad\quad|\quad\quad|\quad\quad|$$
$$CBr{-}CHBr{-}CH\quad CH{-}CHBr{-}CBr$$
$$|\quad\quad|\quad\quad|\quad\quad|$$
$$C_6H_5\quad C_6H_5\quad C_6H_5\quad C_6H_5$$

$\xrightarrow{H_2O}$

$$C_6H_5$$
$$|$$
$$CH{-}CHBr.CO.C_6H_5$$
$$|$$
$$O=P(C_6H_5)_2$$

III

$\xrightarrow{\text{Alc. NaOH}}$

$$C_6H_5.C=CH.COC_6H_5$$
$$|$$
$$O=P(C_6H_5)_2$$

IV

The unsaturated intermediate compound (II) cannot be isolated in the crystalline state ; its reactions with water and bromine are shown. The dibromide is not isolated; with water it gives a mixture of two isomeric monobromoketophosphine oxides, one of which may be obtained by direct bromination of the ketophosphine oxide. Whether the foregoing series of reactions is carried out with benzalacetophenone or benzal-*p*-chloroacetophenone, a higher-melting and a lower-melting bromide may be obtained by treating the intermediate unsaturated compound with bromine. In each case one of the isomers may be prepared by direct bromination of the ketophosphine oxide, the higher-melting isomer resulting in the benzalacetophenone series, and the

[1] Conant, Braverman and Hussey, *J. Amer. Chem. Soc.*, 1923, 45, 165.

lower-melting isomer resulting in the other series. The higher-melting isomer in both series loses hydrogen bromide when treated with alcoholic sodium hydroxide at room temperature and forms an unsaturated ketophosphine oxide (IV), which is reduced by zinc and acetic acid to the saturated oxide. Similar treatment of the lower-melting isomers leads to the isolation of the saturated ketophosphine oxide. The higher-melting isomer from benzalacetophenone, when boiled with an alcoholic solution of potassium acetate, is quantitatively reduced, and the lower-melting isomer of each series can be partially converted into the unsaturated ketophosphine oxide by boiling with pyridine for five hours. The higher- and lower-melting forms are apparently stereoisomers, since both form either the unsaturated or saturated compound, depending upon the reagents employed. From their behaviour towards alcoholic sodium hydroxide the higher-melting isomers apparently have the configuration most suitable for the elimination of hydrogen bromide. Although these compounds have the bromine atom in the β-position to the phosphorus atom, the latter is not eliminated when the compounds are treated with alkaline reagents. This is in striking contrast to the behaviour of the various β-bromophosphinic acids, which easily and quantitatively lose both bromine and phosphorus :

$$\begin{array}{l} C_6H_5.CH\text{—}CHBr.CO.C_6H_5 \\ \quad\quad | \\ C_6H_5.P.OH \\ \quad\quad \| \\ \quad\quad O \end{array} \longrightarrow C_6H_5.CH=CH.CO.C_6H_5 + C_6H_5.PO(OH)_2 + HBr$$

Diphenyl - α - hydroxybenzylphosphine oxide, $C_6H_5.CHOH.PO(C_6H_5)_2$.—5 grams of benzaldehyde are dissolved in 3 grams of glacial acetic acid and 10·4 grams of diphenylchlorophosphine added. After 30 minutes the mixture is poured into water, the gummy precipitate dissolved in ether and the solution washed with sodium hydroxide, dried and evaporated. The oxide crystallises from hot toluene in white crystals, M.pt. 230° C., stable towards mild oxidising agents, but with chromic anhydride in warm sulphuric acid yielding some benzaldehyde.

Diphenyl-α-phenyl-β-benzoylethylphosphine oxide, $(C_6H_5)_2PO.CH(C_6H_5).CH_2.CO.C_6H_5$.—5 grams of benzalacetophenone in 1·5 grams of glacial acetic acid are treated with 5·3 grams of diphenylchlorophosphine and the product worked up as before. About 7·6 grams (77 per cent.) of product result, melting at 227° C. on crystallisation from hot alcohol.

Diphenyl-β-p-chlorobenzoyl-α-phenylethylphosphine oxide, $(C_6H_5)_2PO.CH(C_6H_5).CH_2.CO.C_6H_4Cl$, results in 85 per cent. yield when benzal-*p*-chloroacetophenone is used in the foregoing reaction. It melts at 225° to 226° C.

Diphenyl-α-phenyl-β-bromo-β-benzoylethylphosphine oxide, $(C_6H_5)_2PO.CH(C_6H_5).CHBr.CO.C_6H_5$. — Diphenyl-$\alpha$-phenyl-$\beta$-benzoylethylphosphine oxide may readily be brominated in chloroform solution by heating under reflux for 30 minutes. The resulting product is recrystallised from alcohol and is the higher-melting isomer, M.pt. 187° C. The lower-melting isomer is isolated as follows : Diphenylchlorophosphine (5·3 grams) is added to 5 grams of benzalacetophenone which has been dried over phosphorus pentoxide, and after the addition

of 1·25 grams of acetic anhydride the mixture is allowed to stand for 1 hour. An acetic anhydride solution of bromine is then added and after 10 minutes' standing the whole is poured into water and allowed to stand overnight. The solid is filtered off, dissolved in chloroform and the solution dried. After removal of the solvent the product is recrystallised several times, when 1·2 grams of diphenyl-α-phenyl-β-benzoylethylphosphine oxide, 0·7 gram of the higher-melting bromide and 1·6 grams of a bromo-compound of M.pt. 158° C. are obtained. The last-mentioned is the lower-melting isomer, which is more soluble in alcohol than the higher-melting form, so that separation may be effected by means of this solvent.

Diphenyl-α-phenyl-β-bromo-p-chlorobenzoylethylphosphine oxide, $(C_6H_5)_2PO.CH(C_6H_5).CHBr.CO.C_6H_4Cl$.—A preparation conducted in a similar manner to those already described and using benzal-*p*-chloroacetophenone yields a higher-melting isomer, M.pt. 196° C., and a lower-melting isomer, M.pt. 187° C.

Diphenyl-α-phenyl-β-benzoylvinylphosphine oxide, $(C_6H_5)_2PO.C(C_6H_5)=CH.CO.C_6H_5$, results in 80 per cent. yield when hydrogen bromide is eliminated from the higher-melting isomer of diphenyl-α-phenyl-β-bromo-β-benzoylethylphosphine oxide. 3 grams of the latter (M.pt. 187° C.) are dissolved in hot alcohol, and after cooling to room temperature, concentrated aqueous sodium hydroxide is added. After one hour the mixture is poured into water, acidified and allowed to stand overnight. 2 grams of the oxide result, M.pt. 143° C. The oxide reduces potassium permanganate in acetone solution, but does not combine with bromine or hydrobromic acid in acetic acid solution. Warming with zinc dust and glacial acetic acid reduces the oxide to the corresponding saturated oxide, and dry ozone combines with the oxide in chloroform solution. If the lower-melting isomer of diphenyl-α-phenyl-β-bromo-β-benzoylethylphosphine oxide (M.pt. 158° C.) be treated in exactly the same way a yield of 1·6 grams of diphenyl-α-phenyl-β-benzoylethylphosphine oxide, M.pt. 227° C., is obtained, *i.e.* a replacement of bromine by hydrogen occurs. The higher-melting isomer (0·4 gram), when boiled for 5 hours in methyl alcohol with potassium acetate, yields 0·25 gram of the ketophosphine oxide, but no trace of unsaturated compound, whilst the lower-melting isomer yields a gum.

Diphenyl-α-phenyl-β-p-chlorobenzoylvinylphosphine oxide, $(C_6H_5)_2PO.C(C_6H_5)=CH.CO.C_6H_4Cl$, is obtained from the higher-melting isomer of diphenyl-α-phenyl-β-bromo-*p*-chlorobenzoylethylphosphine oxide (M.pt. 196° C.) by the action of sodium hydroxide and alcohol. The yield is quantitative and the compound crystallises in yellow needles, M.pt. 151° C. Under similar conditions the lower-melting isomer of the β-bromo-acid (M.pt. 187° C.) gives a 95 per cent. yield of ketophosphine oxide, but no trace of unsaturated compound. The higher-melting bromo-acid, when heated with potassium acetate in alcohol solution for three hours, gives a 78 per cent. yield of unsaturated compound, whilst the lower-melting bromo-acid under the same conditions gives a poor yield of unsaturated compound, but no trace of reduction product is obtained.

The Addition of Alkoxy- and Aryloxy-chlorophosphines to Carbonyl Compounds.[1]

Benzaldehyde condenses at ordinary temperatures with phenoxy-dichlorophosphine, and methoxy- and ethoxy-dichlorophosphines in the presence of acetic acid, forming respectively phenyl, methyl and ethyl esters of α-hydroxybenzylphosphinic acid :

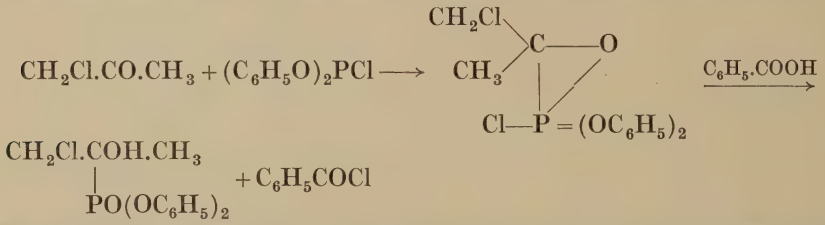
$$C_6H_5.CHO + RO.PCl_2 + 2CH_3COOH = C_6H_5.CHOH.PO(OH)(OR) + 2CH_3COCl$$

The constitution of these esters is shown by converting them into α-hydroxybenzylphosphinic acid by hydrolysis with 15 per cent. aqueous hydrochloric acid and identifying the acid formed by means of its aniline salt.

Phenoxydichlorophosphine condenses with benzalacetophenone in the presence of acetic acid, or better, acetic anhydride, with formation of phenyl β-benzoyl-α-phenylethylphosphinate.

Ethoxydichlorophosphine does not condense normally with benzal-acetophenone, although normal results are noted with benzaldehyde.

Diphenoxychlorophosphine reacts with chloroacetone in the presence of benzoic acid, but not in the presence of acetic acid or acetic anhydride:



$$CH_2Cl.CO.CH_3 + (C_6H_5O)_2PCl \longrightarrow \begin{matrix} CH_2Cl \\ | \\ CH_3-C-O \\ | \quad / \\ Cl-P=(OC_6H_5)_2 \end{matrix} \xrightarrow{C_6H_5.COOH} \begin{matrix} CH_2Cl.COH.CH_3 \\ | \\ PO(OC_6H_5)_2 \end{matrix} + C_6H_5COCl$$

The foregoing curious fact concerning the solvents used in this reaction is assumed to be due to the probability that the speed of the primary addition reaction is very slow, and the diphenoxychlorophosphine is decomposed by the acetic acid or anhydride before it has reacted appreciably with the ketone. Benzoic acid, on the other hand, does not react with the phosphorus derivative at room temperature, hence the reaction can proceed slowly when benzoic acid is present ; as fast as the primary addition product is formed it reacts with the benzoic acid, producing the required diphenyl ester and benzoyl chloride.

Diphenyl α-hydroxybenzylphosphinate, $C_6H_5.CHOH.PO(OC_6H_5)_2$.—8 grams of acetic acid are added to a mixture of 9·2 grams of diphenoxychlorophosphine and 3·9 grams of benzaldehyde. The mixture becomes warm and after standing overnight the crystals are removed, washed with ether and dried, about 4·8 grams being obtained. After crystallisation from methyl alcohol the compound melts at 146° C. It is insoluble in benzene, water or sodium carbonate solution. Boiling with hydrochloric acid hydrolyses it to the phosphinic acid.

Diphenyl α-hydroxyisopropylphosphinate, $(CH_3)_2.COH.PO(OC_6H_5)_2$, results when the benzaldehyde in the foregoing is replaced by acetone. It is best crystallised from petroleum ether, and melts at 113° to 114° C. A small quantity of the *acetyl derivative* of the phosphinate is also produced during the reaction ; it is a crystalline compound, M.pt. 72° to 72·5° C.

[1] Conant, Wallingford and Gandheker, *J. Amer. Chem. Soc.*, 1923, 45, 762.

Diphenyl α - hydroxy - α - methylpropylphosphinate, $C_2H_5.C(CH_3)OH.PO(OC_6H_5)_2$.—This occurs when methyl ethyl ketone is used in the condensation. The ester when recrystallised from alcohol melts at 128·5° C.

Diphenyl α - hydroxy - α - methylbenzylphosphinate, $C_6H_5.C(CH_3)(OH).PO(OC_6H_5)_2$.—Diphenoxychlorophosphine and acetophenone in glacial acetic acid solution yield this ester after standing for 4 days. The compound melts at 143·5° C.

Diphenyl α-hydroxy-β-chloroisopropylphosphinate, $CH_2Cl.C(CH_3)(OH).PO(OC_6H_5)_2$.—This compound, which is prepared by using chloroacetone as indicated on page 142, crystallises in white, cubic crystals, M.pt. 119° C.

The addition of diphenoxychlorophosphine to benzalacetophenone yields *diphenyl α-phenyl-β-benzoylethylphosphinate*, M.pt. 116° to 117° C. Attempts to condense diphenoxychlorophosphine with acetaldehyde, enanthol, cinnamic aldehyde, methyl*iso*propylketone and pinacoline only give oily products which cannot be crystallised.

Phosphorus Derivatives of Dimethylaniline.

Dimethylaminophenyldichlorophosphine, $(CH_3)_2N.C_6H_4.PCl_2$.[1]—A mixture containing 100 grams of phosphorus trichloride and 70 grams of dimethylaniline [2] is treated slowly with 20 grams of anhydrous aluminium chloride, and when the latter has dissolved the whole is boiled for eight hours on a sand-bath, using a calcium chloride guard tube. After cooling the reaction mixture is shaken with petroleum ether (B.pt. 100° C.) until solidification takes place. The solid is filtered off and the filtrate evaporated down until a clear reddish oil remains, the operation being conducted as far as possible in the absence of air. The oil crystallises in large tablets, which are purified by washing with petroleum ether, dissolving in dry ether, distilling off the solvent and crystallising the residue *in vacuo*. The product cannot be distilled at ordinary pressures without decomposition, but boils at about 250° C. at 120 mm. with slight decomposition. The solidified oil consists of thin, pale yellow plates, M.pt. about 66° C., sparingly soluble in petroleum, readily soluble in benzene or phosphorus trichloride. The crystals are deliquescent in air and decomposed by water, the reaction taking place as follows :—

$$(CH_3)_2N.C_6H_4.PCl_2 + 2H_2O = (CH_3)_2N.C_6H_4.P(OH)_2.HCl + HCl$$
$$(CH_3)_2N.C_6H_4.PCl_2 + 3H_2O = (CH_3)_2N.C_6H_5.HCl + P(OH)_3 + HCl$$

The dichlorophosphine may also be prepared by the interaction of phosphorus trichloride and *p*-mercuri-*bis*-dimethylaniline : [3]

$$[(CH_3)_2N.C_6H_4]_2Hg + 2PCl_3 = 2(CH_3)_2N.C_6H_4.PCl_2 + HgCl_2$$

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[1] Schlenk and Michaelis, *Ber.*, 1888, **21**, 1497; Michaelis and Schlenk, *Annalen*, 1890, **260**, 1.

[2] Haniman (*Ber.*, 1876, **9**, 845) states that phosphorus trichloride and dimethylaniline when heated together for some hours at 160° C. evolve methyl chloride. If the reaction mixture is treated with sodium hydroxide and the excess of dimethylaniline removed by boiling with water, the residue crystallises from alcohol as a white, basic body, to which Haniman assigned the formula $[C_6H_4.N(CH_3)_2]_3P$. This product with fuming hydrochloric acid above 160° C. is converted to tri-*m*-aminotriphenylphosphine and triphenylphosphine. The reaction appears to need further investigation.

[3] This Vol., Part I, p. 122.

An ether solution of dimethylaminophenyldichlorophosphine reacts with chlorine to yield a *tetrachloride*, $(CH_3)_2N.C_6H_4.PCl_4$, a pale yellow powder, easily decomposed by moisture. Bromine under similar conditions gives a *chlorobromide*, $(CH_3)_2N.C_6H_4.PCl_2Br_2$, decomposed by water as follows :—

$$3(CH_3)_2N.C_6H_4.PCl_2Br_2 + 8H_2O = (CH_3)_2N.C_6H_3Br_2 + 2(CH_3)_2N.C_6H_4.P(OH)_2 + 4HBr + 6HCl + H_3PO_4$$

Dry hydrogen chloride reacts with the dichlorophosphine to form a *hydrochloride*, but prolonged treatment leads to decomposition, with formation of dimethylaniline hydrochloride and phosphorus trichloride.

Dimethylaminophenylphosphinous acid, $(CH_3)_2N.C_6H_4.P(OH)_2$,[1] is prepared by the action of alcohol on the foregoing dichlorophosphine. It is a colourless crystalline compound, M.pt. 162° C., soluble in water or hot alcohol, and stable towards concentrated hydrochloric acid. Dry distillation causes decomposition with formation of dimethylaniline, phosphine and metaphosphoric acid. The acid yields the following salts : *hydrochloride*, a white crystalline mass, deliquescing in air and forming an oil ; *sodium salt*, crystallising in white tablets containing two molecules of water of crystallisation ; *potassium salt*, a white hygroscopic crystalline mass ; *copper salt*, a pale green powder ; *lead salt*, a white powder. When the acid is caused to react with benzaldehyde in an atmosphere of carbon dioxide at 130° to 170° C., using concentrated hydrochloric acid as a catalyst, a viscous yellow oil results, which corresponds to the formula $[(CH_3)_2N.C_6H_4]_2CH.C_6H_5$; its solution in hydrochloric acid reacts with platinic chloride, forming a platinichloride having the constitution $[(CH_3)_2N.C_6H_4]_2CH.C_6H_5.2H_2PtCl_6$.

Dimethylaminophenylphosphinic acid, $(CH_3)_2N.C_6H_4.PO(OH)_2$, occurs when the sodium salt of the foregoing acid in alcohol solution is treated with mercuric chloride. It melts at 133° C. and is readily soluble in water or alcohol.

Dimethylaminophenyldimethylphosphine, $(CH_3)_2N.C_6H_4.P(CH_3)_2$, is obtained by treating dimethylaminophenyldichlorophosphine with zinc dimethyl in benzene solution in a carbon dioxide atmosphere, the reaction mixture being well cooled during the operation. It is a colourless, strongly refractive liquid, of pungent odour and lighter than water. It boils at 265° C. and above this temperature is converted into the oxide. In air the oil forms a crystalline mass, which after boiling and cooling gives a melting-point of 10° C. Air also converts the phosphine to the *oxide*, $(CH_3)_2N.C_6H_4.P(CH_3)_2O.H_2O$ or $(CH_3)_2N.C_6H_4.P(CH_3)_2(OH)_2$; the change is more rapidly effected by adding mercuric oxide and heating on the water-bath. The oxide separates from hot ether as slender, white needles, M.pt. 62° C., readily soluble in alcohol or chloroform, sparingly soluble in ether. When the phosphine is warmed with sulphur it is converted into the *sulphide*, $(CH_3)_2N.C_6H_4.P(CH_3)_2S$; this forms white needles from alcohol, M.pt. 155° C., becoming yellow on exposure to the air. The *carbon disulphide addition product*, $(CH_3)_2N.C_6H_4.P(CH_3)_2.CS_2$, is a red powder, M.pt. 162° C., sparingly soluble in alcohol. *Dimethylaminophenyltrimethylphosphonium iodide* is prepared from the phosphine in the usual manner ; it crystallises as thick white needles, M.pt. 264° C., which become

[1] Compare American Patent, 1607113.

yellow in air. *Dimethylaminophenyldimethylethylphosphonium iodide* has similar properties to the foregoing compound and melts at 199° C.

Dimethylaminophenyldiethylphosphine, $(CH_3)_2N \cdot C_6H_4 \cdot P(C_2H_5)_2$, isolated from the dichlorophosphine and zinc diethyl, is a colourless liquid, B.pt. 298° C., and re-melts after solidifying at 12·5° C. It is more slowly oxidised in air than the corresponding methyl compound, and has a faint odour ; it readily dissolves in hydrochloric and sulphuric acids. Its *oxide* forms thick transparent needles, M.pt. 65° C. ; the *sulphide* separates as white crystals, M.pt. 148° C., and the *carbon disulphide addition product* yields red plates, M.pt. 107° C.

Dimethylaminophenyldiethylmethylphosphonium iodide is a white mass, M.pt. 186° C., readily soluble in chloroform, insoluble in ether ; the corresponding *ethiodide* separates as thick white needles, M.pt. 180° C.

Dimethylaminophenyldiphenylphosphine, $(CH_3)_2N \cdot C_6H_4 \cdot P(C_6H_5)_2$.—One molecular proportion of dimethylaminophenyldichlorophosphine, two molecular proportions of chlorobenzene and the requisite quantity of sodium are allowed to react in benzene solution. The resulting phosphine melts at 152° C. and is readily soluble in benzene, less soluble in alcohol or ether. It is only a weak base, and is precipitated from its solution in concentrated hydrochloric acid by water. When heated in a sealed tube for eight hours with concentrated hydrochloric acid at 230° C. it reacts as follows :—

$$(CH_3)_2N.C_6H_4.P(C_6H_5)_2 + HCl = (CH_3)_2N.C_6H_5 + (C_6H_5)_2PCl$$
$$2(C_6H_5)_2PCl + 2H_2O = (C_6H_5)_2PH + (C_6H_5)_2PO.OH + 2HCl$$

Oxidation by boiling with ferric chloride yields the *oxide* as a white, crystalline mass, M.pt. 183·5° C., readily soluble in alcohol or chloroform, insoluble in water. The *sulphide*, obtained in the usual manner, forms fine, yellow needles, M.pt. 183° C., readily soluble in alcohol or chloroform. *Dimethylaminophenyldiphenylmethylphosphonium iodide*, $(CH_3)_2N.C_6H_4.P(C_6H_5)_2(CH_3)I$, is an oil, which yields a *hydroxide* in the form of a strongly alkaline deliquescent mass. When dissolved in hydrochloric acid and treated with platinic chloride the phosphine forms a *platinichloride*, $[(CH_3)_2N.C_6H_4.P(C_6H_5)_2.HCl]_2PtCl_4$, a yellow powder, crystallising from alcohol in orange plates. Prolonged boiling of the hydroxide with water, or better, the addition of silver oxide or solid potassium hydroxide, removes benzene from the molecule :

$$(CH_3)_2N.C_6H_4.P(C_6H_5)_2(CH_3)OH = (CH_3)_2N.C_6H_4.P(C_6H_5)(CH_3)O + C_6H_6$$

The *oxide* thus formed dissolves in the usual solvents and forms shining crystals, M.pt. 146° C.

Hexamethyltriaminotriphenylphosphine, $[(CH_3)_2N.C_6H_4]_3P$, occurs as a by-product in the preparation of dimethylaminophenyldichlorophosphine, being present in the residue insoluble in petroleum ether. It forms colourless, slender needles, turning blue in air, melting at about 273° C., and readily dissolving in hot ether, hot alcohol or chloroform.

Diethylaminophenyldichlorophosphine, $(C_2H_5)_2N.C_6H_4.PCl_2$.—This is obtained when the dimethylaniline in the corresponding dimethyl preparation is replaced by diethylaniline. The product is a reddish oil, easily soluble in benzene, ether or alcohol.

Methylbenzylaminophenyldichlorophosphine, $(CH_3)(C_6H_5.CH_2)N.C_6H_4.PCl_2$, is a pale reddish oil. It forms a *phosphinous acid*,

$(CH_3)(C_6H_5.CH_2)N.C_6H_4.P(OH)_2$, crystallising from water or dilute alcohol in small, slender needles, turning green in air and melting at 96° C. The *sodium salt* crystallises in glistening white needles or plates, M.pt. 233° C., containing two molecules of water of crystallisation.

Ethylbenzylaminophenyldichlorophosphine, $(C_2H_5)(C_6H_5.CH_2)N.C_6H_4.PCl_2$, is an oil having similar properties to the foregoing compound.

Methylphenylaminophenyldichlorophosphine, $(CH_3)(C_6H_5)N.C_6H_4.PCl_2$, separates as a viscous, transparent oil, which cannot be distilled without decomposition even *in vacuo*. Sodium hydroxide converts it into the *sodium salt* of the *phosphinous acid*. This salt crystallises in plates containing two molecules of water of crystallisation and melting at 265° C.; it readily dissolves in water, is less soluble in alcohol and insoluble in chloroform or benzene. Hydrochloric acid transforms the sodium salt to the free *phosphinous acid*, which separates from water in small needles and from alcohol in pearly plates, M.pt. 150·5° C., easily soluble in benzene or chloroform.[1]

Derivatives of Dibenzylmethane and Hydroxymethylene Camphor.

Dibenzylmethanephosphinic acid, $(C_7H_7)_2CH.PO(OH)_2$, occurs when hydriodic acid and amorphous phosphorus react with dibenzyl ketone.[2] It crystallises as large, thick needles, M.pt. 142° C., readily soluble in alcohol or ether, sparingly soluble in cold water. When the acid (1 mol.) is heated with phosphorus pentachloride (2 mols.) it yields an *oxychloride*, a viscous, transparent oil, B.pt. 228° C. at 20 mm., density 1·036 at 15° C., water reconverting this into the acid. The acid and oxychloride in benzene solution give *dibenzylmethanephosphinoxide*, $(C_7H_7)_2CH.PO_2$, which crystallises in white tablets, M.pt. 151° C. Concentrated ammonium hydroxide converts the oxychloride into *dibenzylmethanephosphinamic acid*, $(C_7H_7)_2CH.P(OH)NH_2$, consisting of white plates, sintering at 230° C. and melting at 244° C., the *silver salt* being a white precipitate. The following other derivatives of dibenzylmethanephosphinic acid are known: *anilide*, $(C_7H_7)_2CH.PO(NH.C_6H_5)_2$, white needles, M.pt. 196° C., readily soluble in alcohol, hot benzene or chloroform; *phenylhydrazide*, $(C_7H_7)_2CH.PO(NH.NH.C_6H_5)_2$, white needles, M.pt. 164° C.; *diethyl ester*, a viscous liquid, B.pt. 240° C. at 20 mm.; *diphenyl ester*, hard, white prisms, M.pt. 120° C.; *ditolyl ester*, M.pt. 131° C.

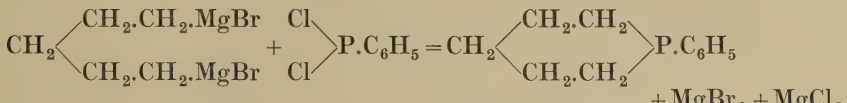
Hydroxymethylene camphor phosphinic acid, $C_{10}H_{14}O=CH.PO(OH)_2$, is isolated as a by-product in the preparation of hydroxymethylene camphor by treating oxymethylene camphor (3 mols.) with phosphorus trichloride (2 mols.). It crystallises with half a molecule of water, which may be expelled at 110° C. The *ammonium*, *silver* and *lead salts* are known, also the following derivatives: *oxychloride*, $C_{10}H_{14}O=CH.POCl_2$, white tablets, M.pt. 51° C., B.pt. 175° to 180° C., decomposed by water; *aniline salt*, M.pt. 195° to 196° C.; *anilide*, slender yellow needles, M.pt. 227° to 228° C.; *p-toluidide*, M.pt. 210° C.; *p-phenetidide*, M.pt. 137° C.; *diethyl ester*, B.pt. 195° to 205° C. at 20 mm., decomposed by water.

[1] For *p*-dimethylaminotolylphosphinous acid, see American Patent, 1635169.

[2] Michaelis and Fleming, *Ber.*, 1901, 34, 1291.

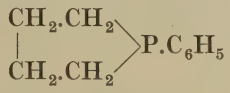
Heterocyclic Rings containing Phosphorus.

The heterocyclic ring compounds of phosphorus are similar to those already described for tin, lead [1] and arsenic.[2] The formation of a phosphorus ring system is shown by the following equation :—



$$CH_2\langle{}^{CH_2.CH_2.MgBr}_{CH_2.CH_2.MgBr} + {}^{Cl}_{Cl}\rangle P.C_6H_5 = CH_2\langle{}^{CH_2.CH_2}_{CH_2.CH_2}\rangle P.C_6H_5 + MgBr_2 + MgCl_2$$

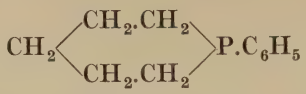
Phenylcyclotetramethylenephosphine,[3]



To the magnesium compound obtained from 50 grams of 1 : 4-dibromobutane in 200 c.c. of absolute ether, 25 grams of phenyldichlorophosphine diluted with three volumes of ether are slowly added with brisk stirring and ice-cooling. A violent reaction ensues, and on its completion the ether is distilled off in a stream of hydrogen and the residue distilled from a metal-bath in hydrogen up to 350° C. at 20 mm. pressure. The distillate is fractionated in a carbon dioxide atmosphere, the pure product boiling at 132° to 133° C. at 16 to 18 mm. It is a transparent oil having a strong, characteristic phosphine odour, and gives the following physical constants : density, 1·0502 at 0° C., 1·0429 at 10° C., 1·0354 at 20° C., 1·0281 at 30° C., 1·0208 at 40° C., 1·0335 at 22·5° C. ; n_D 1·5894 at 22·5° C. ; $n_F - n_C$ 0·02163 at 22·5° C. It does not fume and is only slowly oxidised in air at ordinary temperatures. In water it is only slightly soluble, but dissolves readily in most organic solvents ; it readily reduces neutral or faintly acid solutions of silver nitrate. With *mercuric chloride* it forms an *addition product*, $C_{10}H_{13}P.HgCl_2$, separating from hot benzene in rhombic crystals, M.pt. 143° to 144° C. with decomposition. This product is sparingly soluble in water, alcohol, benzene or ether, readily soluble in pyridine and its homologues. The phosphine forms the usual *addition products* with *carbon disulphide*, *sulphur* and *platinic chloride*, also *compounds* with *carbon tetrachloride*, *hexachloroethane*, *arsenic trichloride*, *antimony trichloride*, *bismuth trichloride*, *silicon tetrachloride*, *triethylsilicon chloride*, *phenyldichloroarsine*, *diphenylchloroarsine*, *tin tetrabromide* and *tin diphenyl dibromide*. These compounds are only sparingly soluble. The following derivatives are obtained in the usual manner : *Phenylcyclotetramethylenemethylphosphonium iodide*, $(CH_2)_4 > P(C_6H_5)(CH_3)I$, a colourless oil ; *phenylcyclotetramethylene-ethylphosphonium iodide*, a pale yellow crystalline powder, M.pt. 122° C., readily soluble in water or alcohol, less soluble in ether or petroleum ether ; *phenylcyclotetramethylene-n-propylphosphonium iodide*, a snow-white crystalline powder, M.pt. 153° to 154° C. ; *phenylcyclotetramethylene-sec.-propylphosphonium iodide*, pale yellow crystals tending to be hygroscopic and having no definite melting-point ; *iso*amyl iodide and ethylene bromide give yellow oils which cannot be crystallised.

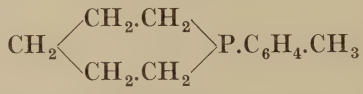
[1] This Vol., Part I, p. 352.
[2] This Vol., Part II, p. 410.
[3] Grüttner and Krause, *Ber.*, 1916, **49**, 437.

Phenylcyclopentamethylenephosphine,[1]



is prepared by substituting the 1 : 4-dibromobutane in the preceding preparation by 1 : 5-dibromopentane. It is a colourless oil of characteristic phosphine odour, B.pt. 154° to 155° C. at 22 to 24 mm., fuming in air but not appreciably oxidised. It readily dissolves in alcohol, benzene, ether or petroleum ether, is sparingly soluble in water, and reduces neutral or dilute nitric acid solutions of silver nitrate. The *mercurichloride* melts at 172° C. and the *ethiodide* at 178° C.

p-Tolylcyclopentamethylenephosphine,



obtained from *p*-tolyldichlorophosphine, boils at 167° to 168° C. at 24 mm., and resembles the preceding compound in properties. Chlorine reacts with it, causing partial decomposition with formation of some 1 : 5-dichloropentane. The *mercurichloride* melts at 157° C.; the *methiodide* is an oil which cannot be induced to crystallise, but the *ethiodide* forms white crystals, M.pt. 163° to 164° C.

Compounds of the Type RP = PR.

Phosphobenzene, $C_6H_5.P=P.C_6H_5$.—10 grams of phenylphosphine in a well-cooled flask are treated dropwise with 10 grams of phenyldichlorophosphine, the operation being conducted in an atmosphere of hydrogen.[2] A violent reaction occurs, accompanied by foaming; the reaction is completed finally by gentle warming, when a solid product results. This is treated with water and alcohol-free ether until a portion when oxidised by nitric acid gives no reaction with silver nitrate. The ether is then as far as possible poured off, and the remainder driven off by heating on the water-bath in a current of hydrogen. A pale yellow powder results, insoluble in alcohol, hot water or ether, readily soluble in hot benzene.

Air oxidises phosphobenzene to the *oxide*, $(C_6H_5.P)_2O$, whilst chlorine causes inflammation unless diluted with carbon dioxide, when phenyldichlorophosphine occurs :

$$C_6H_5.P=P.C_6H_5+2Cl_2 \longrightarrow 2C_6H_5.PCl_2$$

The oxide under similar conditions yields a mixture of phenyldichlorophosphine and phenyl phosphorus oxychloride. Dilute nitric acid transforms phosphobenzene with violence into phenylphosphinous acid, whilst concentrated nitric acid gives the phosphinic acid :

$$C_6H_5.P=P.C_6H_5+\ O_2+2H_2O \longrightarrow 2C_6H_5.P(OH)_2$$
$$C_6H_5.P=P.C_6H_5+2O_2+2H_2O \longrightarrow 2C_6H_5.PO(OH)_2$$

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[1] Grüttner and Wiernik, *Ber.*, 1915, 48, 1473.
[2] Köhler and Michaelis, *Ber.*, 1877, 10, 807.

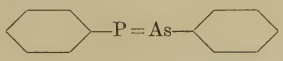
Concentrated hydrochloric acid gives a mixture of phenylphosphine and phenyldichlorophosphine :

$$C_6H_5.P=P.C_6H_5+2HCl \longrightarrow C_6H_5.PH_2+C_6H_5.PCl_2$$

When phosphine is dried over potassium hydroxide and passed through phenyldichlorophosphine for several days, a thick, pale yellow, viscous liquid results.[1] This becomes turbid on exposure to the air, and addition of water or alcohol causes the precipitation of a yellow solid. The product is triturated in a mortar, washed with alcohol and dried over sulphuric acid, and the following formula, based upon analytical data, is assigned to it, $C_6H_5.P=POH$. It is insoluble in water or alcohol, sparingly soluble in ether, readily soluble in carbon disulphide. At ordinary temperatures it is stable in air, but it inflames on heating and burns with a sooty flame. With warm nitric acid red fumes are evolved and an intense yellow solution results, but prolonged warming yields a colourless solution containing phenylphosphinic and phosphoric acids :

$$C_6H_5.P=P.OH+2H_2O+2O_2 \longrightarrow C_6H_5.PO(OH)_2+PO(OH)_3$$

Phospho-arsenobenzene,[2]



is obtained by the interaction of phenyldichlorophosphine and phenylarsine :

$$C_6H_5.PCl_2+H_2As.C_6H_5 = C_6H_5.P=As.C_6H_5+2HCl$$

Phenylarsine, 7·35 grams, and 8·66 grams of phenyldichlorophosphine are mixed in 30 c.c. of ether. The ether is removed at 50° C. on the water-bath, and a violent evolution of hydrogen chloride suddenly takes place. A yellow crystalline mass consisting of fine needles results. After washing with alcohol and ether the product melts at 181° C. Recrystallisation from benzene causes decomposition into arsenobenzene and phosphobenzene. The latter appears to melt at 149° to 150° C.[3]

Phosphinic Acids derived from Triarylmethoxyphosphorus Dichlorides.

Triphenylmethylphosphinic acid, $(C_6H_5)_3C.PO(OH)_2$,[4] occurs when alcoholic potassium hydroxide reacts with triphenylmethoxyphosphorus dichloride. The hydrolysis is abnormal and the phosphorus changes from the tervalent to the pentavalent state :

$$(C_6H_5)_3CO.PCl_2 \xrightarrow[\text{Alc.KOH}]{} (C_6H_5)_3C.PO(OC_2H_5)(OK)$$

The pure acid is most conveniently isolated as follows : The precipitate obtained on acidifying the solution of the crude acid in potassium hydroxide is dried in a steam-oven, then boiled for an hour with a

[1] Michaelis, *Ber.*, 1875, 8, 499.
[2] Steinkopf and Dudek, *Ber.*, 1929, 62, [B], 2494.
[3] British Patent 9234 (1915) deals with arsenophosphorus compounds.
[4] Boyd and Chignell, *Trans. Chem. Soc.*, 1923, 123, 813; 1924, 125, 1477; compare Arbuzoff and Arbuzoff, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 217.

mixture of acetic acid and concentrated hydriodic acid (3 grams of phosphinic acid, 15 c.c. of acetic acid and 8 c.c. of hydriodic acid). Large prismatic crystals of triphenylmethylphosphinic acid separate as the solution cools. These are washed with dilute sulphurous acid, then with dilute hydrochloric acid, followed by a little alcohol, and finally with ether. Recrystallisation from glacial acetic acid or benzene gives a product, M.pt. 275° C. If five to six molecular proportions of potassium hydroxide per molecule of phosphorus chloride be used in place of three proportions, the yield may be raised to about 80 per cent.

The acid reacts with phosphorus pentachloride at 70° C. giving triphenylchloromethane, M.pt. 106° to 109° C.[1] The *dipotassium salt*, $(C_6H_5)_3C.PO(OK)_2.3H_2O$, forms lustrous leaflets, and the *barium salt*, $(C_6H_5)_3C.PO_3Ba.4H_2O$, is a white precipitate. The *monoethyl ester*, $(C_6H_5)_3C.PO(OC_2H_5)(OH)$, melts at 227° to 232° C. The *triphenylmethoxyphosphorus dichloride* required for the foregoing preparation is obtained by the action of phosphorus trichloride on triphenylcarbinol.

The following is a general method of preparation for the triarylmethoxyphosphorus dichlorides [2] and for their conversion to triarylmethylphosphinic acids: One gram-molecule of the triarylcarbinol is slowly added to about two molecular proportions of phosphorus trichloride cooled in ice, and the mixture kept at room temperature for at least forty-eight hours. The resulting solid is treated with ice and water, digested in the cold during several days first with ammonium hydroxide and afterwards with sodium carbonate solution, washed free from alkali, dried in a vacuum, and crystallised from a suitable solvent. On acidification of the alkaline filtrate a small quantity of triarylmethylphosphinic acid is precipitated, but in order to obtain the maximum yield of the phosphinic acid, formed as a by-product in the preparation of the triarylmethoxyphosphorus dichloride, it is usually necessary to carry out the digestion with ammonium hydroxide on a steam-bath. The triarylmethoxyphosphorus dichlorides are all soluble in cold concentrated sulphuric acid with evolution of hydrogen chloride, and from the strongly coloured solutions the carbinols are precipitated on addition of water. The transformation of these dichlorides to acids takes place when the chloride (1 mol.) is heated on a water-bath with potassium hydroxide (4·5 to 5 mols.) and ethyl alcohol (about 99 per cent.). Heating is continued for a short time after potassium chloride has separated, and then water is added and the alcohol evaporated off on the steam-bath. The aqueous solution is boiled for some time and, when cold, is filtered from solid matter and strongly acidified with hydrochloric acid. The precipitated mono-ethyl ester of the triarylmethylphosphinic acid is refluxed for an hour with a mixture of glacial acetic acid and concentrated hydriodic acid. On cooling, the phosphinic acid separates and is washed and weighed after drying at 110° C. Addition of water to the filtrate gives a further small quantity of acid. From 5 grams of triphenylmethoxyphosphorus dichloride, 3·8 grams of potassium hydroxide and 38 c.c. of alcohol, the yield of triphenylmethylphosphinic acid was 4·079 grams, or a 91 per cent. yield. All the acids obtained by this method are dibasic, this fact being established by preparation of the corresponding dipotassium salts and by electrometric titration.

By use of the foregoing method the following dichlorides and their

[1] Hatt, *J. Chem. Soc.*, 1929, p. 2412. [2] Boyd and Chignell, *loc. cit.*

respective acids have been isolated: *p-Chlorotriphenylmethoxyphosphorus dichloride*, $ClC_6H_4.C(C_6H_5)_2O.PCl_2$, colourless crystals, M.pt. 161·5° C., *p-chlorotriphenylmethylphosphinic acid*, $ClC_6H_4.C(C_6H_5)_2PO(OH)_2$, minute crystals, M.pt. 273° C., and the *dipotassium salt*, small lustrous plates; *p-bromotriphenylmethoxyphosphorus dichloride*, $BrC_6H_4.C(C_6H_5)_2O.PCl_2$, M.pt. 163° C., *p-bromotriphenylmethylphosphinic acid*, $BrC_6H_4.C(C_6H_5)_2PO(OH)_2$, colourless crystals, M.pt. 297° C., containing a molecule of acetic acid, which is retained after prolonged keeping in a vacuum, but may be driven off by heating for several hours at 100° C., the *dipotassium salt*, glistening plates, and the *barium salt*, a heavy white precipitate; *diphenyl-p-anisylmethoxyphosphorus dichloride*, $CH_3O.C_6H_4.C(C_6H_5)_2O.PCl_2$, minute white crystals, M.pt. 180° C., and *diphenyl-p-anisylmethylphosphinic acid*, $CH_3O.C_6H_4.C(C_6H_5)_2PO(OH)_2$, M.pt. 210° C.; *diphenyl-m-anisylmethoxyphosphorus dichloride*, $CH_3O.C_6H_4.C(C_6H_5)_2O.PCl_2$, minute, snow-white crystals, M.pt. 122° to 124° C.; *m-hydroxytriphenylmethylphosphinic acid*, $HO.C_6H_4.C(C_6H_5)_2PO(OH)_2$, fine white needles sintering at 239° C. and melting at 248° C., the *disodium salt*, lustrous plates, the *benzoyl derivative*, a white powder, the *disilver salt* of the benzoylated acid, a white precipitate, and the acid formed by methylation of the free acid, M.pt. 197° C.; *diphenyl-α-naphthylmethoxyphosphorus dichloride*, $C_{10}H_7.C(C_6H_5)_2O.PCl_2$, white microscopic crystals, M.pt. 171° to 172° C., *diphenyl-α-naphthylmethylphosphinic acid*, $C_{10}H_7.C(C_6H_5)_2PO(OH)_2$, fine needles, M.pt. 256° C., and the *dipotassium salt*, lustrous plates; *diphenyl-β-naphthylmethoxyphosphorus dichloride*, $C_{10}H_7.C(C_6H_5)_2O.PCl_2$, small white crystals, M.pt. 194° C., *diphenyl-β-naphthylmethylphosphinic acid*, $C_{10}H_7.C(C_6H_5)_2PO(OH)_2$, colourless needles, M.pt. 247·5° C., the *dipotassium salt* being known; *p-nitrotriphenylmethoxyphosphorus dichloride*, $NO_2.C_6H_4.C(C_6H_5)_2O.PCl_2$, colourless crystals, M.pt. 188·5° C.; *diphenyl-p-tolylmethoxyphosphorus dichloride*, $CH_3.C_6H_4.C(C_6H_5)_2O.PCl_2$, minute colourless crystals, M.pt. 193° C., *diphenyl-p-tolylmethylphosphinic acid*, $CH_3.C_6H_4.C(C_6H_5)_2PO(OH)_2$, M.pt. 254° C., which may contain one molecule of water or acetic acid of crystallisation, according to the method of purification, and the *dipotassium salt*, pearly leaflets.

An attempt has been made [1] to explain the mechanism of the reaction occurring when triphenylmethoxyphosphorus dichloride is converted into triphenylmethylphosphinic acid by observing the rate of formation of sodium chloride, and also by examination of the phosphorus-containing products. Using 2·5*N* alcoholic sodium ethoxide, the removal of chlorine atoms proceeds in definite stages. The first halogen is rapidly removed, the velocity being influenced chiefly by the rate of dissolution of the phosphorus dichloride in alcohol. The final product is *ethyl hydrogen triphenylmethylphosphinate*, M.pt. 259° C., which yields a *silver salt* as a white crystalline precipitate. The course of the reaction is given as follows:—

$$(C_6H_5)_3CO.PCl_2 \longrightarrow \underset{\text{(I)}}{(C_6H_5)_3CO.PCl(OC_2H_5)} \longrightarrow \underset{\text{(II)}}{}$$

$$\underset{\text{(III)}}{(C_6H_5)_3C.POCl(ONa)} \longrightarrow (C_6H_5)_3C.PO(OC_2H_5)(ONa)$$

[1] Hatt, *J. Chem. Soc.*, 1929, p. 2412.

This hypothesis is supported by the isolation at the appropriate stage of *triphenylmethylchlorophosphinic acid* (III), M.pt. 233° to 234° C., which forms an *aniline salt*, M.pt. 182° to 182·5° C., or 151° to 156° C. on rapid heating, and containing one molecule of alcohol of crystallisation; the *quinoline salt* forms large, colourless crystals, M.pt. 181·5° to 182·5° C. When 0·2 to 0·5*N* sodium ethoxide is employed, the *chloro-ester* (II) results in 85 per cent. yield and melts at 135° to 137° C. Heating with 2*N* sodium ethoxide solution or hydriodic-acetic acid mixture transforms II into III.

In concentrated solutions an alternative course exists :

$(C_6H_5)_3CO.PCl_2 \longrightarrow (C_6H_5)_3CO.PCl(OC_2H_5) \longrightarrow (C_6H_5)_3C.PO(OC_2H_5)_2 \longrightarrow (C_6H_5)_3C.PO(OC_2H_5)(ONa)$

This course of reaction is indicated by the isolation of *diethyl triphenylmethylphosphinate*, M.pt. 120° to 121° C., in 20 per cent. yield when 4*N* solutions of sodium ethoxide are used. This ester undergoes sulphonation with concentrated sulphuric acid, but hot aqueous sulphuric acid first causes hydrolysis into the *monoethyl ester*, then into the phosphinic acid itself.

Aliphatic Phosphino-acids and their Derivatives.

Although arsinoacetic acid is readily produced from chloroacetic acid and an excess of sodium arsenite, the analogous reaction does not take place with sodium phosphite. Sodium salts of phosphorous and chloroalkyl acids when brought into contact react with a partial conversion of the phosphorus into the quinquevalent state, and, apparently, the production of an unstable ester-like derivative of glycollic and phosphorous acids which cannot be isolated. Methyl iodide and sodium phosphite yield the readily hydrolysed methyl phosphite unaccompanied by methylphosphinic acid.

Ethyl phosphinoacetate,[1] $C_2H_5O_2C.CH_2.PO(OC_2H_5)_2$, occurs when sodium diethylphosphite (obtained from phosphorus trichloride and ethyl alcohol, followed by treatment with sodium in the presence of ether) reacts with ethyl chloroacetate. It may also be obtained in 95 per cent. yield when sodium ethoxide, diethylphosphite and ethyl chloroacetate react in absolute alcohol solution ;[2] in other solvents, such as ether or light petroleum, the yields are considerably smaller. The ester boils at 140° to 141° C. at 9 to 10 mm.,[3] and reacts with ammonium hydroxide to form an *amide*, $NH_2.CO.CH_2.PO(OC_2H_5)_2$, white glistening needles, M.pt. 78° to 80° C. (corr.).[4]

P-Monoethyl phosphinoacetate, $HOOC.CH_2.PO(OH)(OC_2H_5)$, is formed when the preceding compound is hydrolysed by boiling with sodium hydroxide or dilute hydrochloric acid. It also occurs when methyl diethyl phosphinoacetate, $CH_3O_2C.CH_2.PO(OC_2H_5)_2$, B.pt. 131·5° to 132° C. (corr.) at 9 mm., is hydrolysed. *Sodium* and *silver salts* of the monoester are known.

C-Monoethyl phosphinoacetate, $C_2H_5O_2C.CH_2.PO(OH)_2$.— Phosphinoacetic acid (3 grams) is boiled for 4 hours with 15 grams of 5 per cent. hydrochloric acid in absolute alcohol solution, and the

[1] Nylén, *Ber.*, 1924, 57, [B], 1023.
[2] Arbusoff and Kamaï, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 619.
[3] Compare Arbusoff, *ibid.*, 1906, 38, 161, 293, 687.
[4] Nylén, *loc. cit.*

mixture then evaporated on the water-bath. The residue is dried for several days *in vacuo* over potassium hydroxide and phosphorus pentoxide, a viscous syrup resulting. This is very soluble in water, alcohol or ether, insoluble in benzene. The *neutral sodium salt* solution gives white precipitates with salts of zinc, manganese, lead or silver. Copper sulphate gives a blue voluminous precipitate.

Phosphinoacetic acid, $HOOC.CH_2.PO(OH)_2$, is prepared by heating the triethyl ester with 1 per cent. hydrochloric acid, first on a water-bath for five hours, then in a sealed tube at 140° to 160° C. The solution is evaporated to dryness and the residue recrystallised from acetic acid or water, when shining prisms or rhomboids are obtained, M.pt. 142° to 143° C. (corr.). The acid is readily soluble in water, alcohol, acetone or acetic acid, insoluble in ether, benzene or chloroform. In warm weather the acid is hygroscopic. It decomposes *in vacuo* at about 280° C. It behaves towards thymolphthalein as a tribasic acid. The following salts are known: *Disodium hydrogen salt, diammonium hydrogen salt, potassium dihydrogen salt, normal calcium salt* (H_2O), *normal barium salt* (H_2O), *copper hydrogen salt* ($2H_2O$), *normal copper salt* ($8H_2O$), *normal manganese salt* ($6H_2O$), *normal zinc salt* (H_2O), *normal lead salt, normal silver* and *disilver hydrogen salts.*

Phosphinoacetyl trichloride, $ClOC.CH_2.POCl_2$, is the product of reaction between the foregoing acid and phosphorus pentachloride. It is a colourless liquid, B.pt. 79° to 80° C. at 1 to 2 mm. It has a faint odour resembling that of phosphorus pentachloride, and is heavier than water, by which it is slowly decomposed.

Phosphinoacetic trianilide, $C_6H_5.NH.CO.CH_2.PO(NH.C_6H_5)_2$, is the condensation product of the trichloride and aniline. It separates from alcohol as colourless needles, M.pt. 191·5° to 192·5° C. (corr.), and dissolves in warm alcohol, ether, or benzene, but is insoluble in water. The *tri-p-toluidide* forms colourless needles, M.pt. 190° to 192° C. (corr.).

Phosphinoacethydrazide, $NH_2.NH.CO.CH_2.PO(OH)_2$. — Ethyl phosphinoacetate is transformed to the hydrazide by boiling with hydrazine hydrate. With *acetone* the hydrazide forms the *compound,* $(CH_3)_2C=N.NH.CO.CH_2.PO(OH)_2$, melting with decomposition at 185° to 186° C.

Ethyl phosphinoformate, $C_2H_5O_2C.PO(OC_2H_5)_2$, obtained from triethylphosphite, sodium diethylphosphite, and ethyl chloroformate, is a colourless liquid, B.pt. 122·5° to 123° C. (corr.) at 8 mm.[1] It yields an *amide,* $NH_2.CO.PO(OC_2H_5)_2$, M.pt. 134° to 135° C. (corr.). The ester is hydrolysed by boiling water or acids to carbonic and phosphorous acids, whereas with sodium hydroxide the main product is *sodium phosphinoformate,* which salt is neutral towards thymolphthalein and alkaline towards phenolphthalein. The *phosphinoformates* of *zinc* ($12H_2O$), *manganese* ($12H_2O$), *copper* ($8H_2O$), *lead* and *silver* are known.

Ethyl benzyldiethylphosphinoacetate,[2] $C_2H_5O_2C(C_7H_7)CH.PO(OC_2H_5)_2$, obtained in the usual manner, boils at 180° C. at 3 mm., and *benzylphosphinoacetic acid,* $HOOC.CH(C_7H_7).PO(OH)_2$, melts at 137° to 145° C.

α-Phosphinopropionic acid,[3] $HOOC.CH(CH_3).PO(OH)_2$.—Ethyl

[1] Compare Arbusoff, *loc. cit.*
[2] Arbuzoff and Razumoff, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 623.
[3] Nylén, *loc. cit.*

α-phosphinopropionate, B.pt. 130·5° to 132·5° C. at 10·5 mm., prepared from the ethyl ester of α-bromopropionic acid and triethyl phosphite, is heated with water at 140° to 150° C., filtered and the filtrate treated with lead acetate. This precipitates the *lead salt* of the acid, from which the free acid is obtained as a hygroscopic mass melting indefinitely at 75° to 95° C. The normal *silver* and *manganese salts* are known.

Ethyl α-diethylphosphinopropionate, $C_2H_5O_2C.CH(CH_3).PO(OC_2H_5)_2$,[1] occurs along with α-diethylphosphinopropionic acid when ethyl sodiophosphinoacetate is condensed with methyl iodide. The acid cannot be distilled without decomposition; the ester boils at 127° C. at 5 mm. These products on hydrolysis yield α-phosphinopropionic acid, M.pt. 119° to 132° C. (note M.pt. already given). Better yields of the phosphinopropionic ester are obtained using the potassium salt of ethyl phosphinoacetate in the preparation, no diethylphosphinopropionic acid being obtained in this case.

Ethyl β-phosphinopropionate,[2] $C_2H_5O_2C.CH_2.CH_2.PO(OC_2H_5)_2$, is obtained by the successive addition of ethyl phosphite and ethyl β-iodopropionate to sodium ethoxide suspended in ether. The yield is about 35 per cent. and the ester is a colourless, odourless liquid, B.pt. 149·5° to 150° C. (corr.) at 10 mm., density 1·1021 at 16·7° C. It dissolves in water and organic solvents. Alcoholic ammonia converts it into the corresponding *C-amide*, M.pt. 61° to 62·5° C. (corr.), crystallising in needles, soluble in water, alcohol or warm benzene, sparingly soluble in warm ether.

β-Phosphinopropionic acid, $HOOC.CH_2.CH_2.PO(OH)_2$, is the hydrolysis product of the foregoing ester. It forms rectangular prisms, M.pt. 178° to 180° C. (corr.). The *disilver salt* of the *P-monoethyl ester*, $CO_2Ag.CH_2.CH_2.PO(OC_2H_5)(OAg)$, is known. The acid is converted by ethyl alcohol and hydrogen chloride into the *C-monoethyl ester*, $C_2H_5O_2C.CH_2.CH_2.PO(OH)_2$, glistening plates, M.pt. 64·5° to 66° C. (corr.), which forms *zinc*, *manganese*, *calcium*, *silver* and *copper salts*. β-Phosphinopropionic acid itself forms the following salts: *disodium hydrogen salt*, *normal calcium salt* (H_2O), *normal barium salt* ($6H_2O$), *zinc salt* ($3H_2O$), *manganous salt* ($7H_2O$), *lead* and *silver salts*.

γ-Phosphinobutyronitrile ethyl ester, $CN.CH_2.CH_2.CH_2.PO(OC_2H_5)_2$, is prepared by the condensation of sodium diethyl phosphite with γ-chlorobutyronitrile in ether solution. It boils at 163° to 164° C. at 8 mm. and has a density of 1·0885 at 17° C.

γ-Phosphino-n-butyric acid, $HOOC.CH_2.CH_2.CH_2.PO(OH)_2$. —The preceding nitrile is hydrolysed by heating with 20 per cent. hydrochloric acid on the water-bath for ten hours, followed by three hours' heating in an autoclave at 140° to 150° C. It crystallises from water in prisms or rhombic crystals, sintering at 122° C. and melting at 127° to 128° C. (corr.). It forms the following salts: *normal barium salt* ($6H_2O$), *calcium salt*, *copper salt* ($4H_2O$), *lead salt*, *silver salt*, *manganous hydrogen salt* (H_2O) and *zinc hydrogen salt* (H_2O). The *C-monoethyl ester*, $C_2H_5O_2C.CH_2.CH_2.CH_2.PO(OH)_2$, separates as rhombic crystals, M.pt. 76° to 77° C., and forms *sodium*, *zinc*, *manganese*, *copper*, *calcium*, *lead* and *silver salts*.[3]

[1] Arbuzoff and Razumoff, *loc. cit.* [2] Nylén, *Ber.*, 1926, 59, [B], 1119.

[3] German Patent 299992 (*Chem. Zentr.*, 1917, ii, 510) deals with the production of organic compounds of phosphorus. Unsaturated hydroxy-fatty acids of high molecular weight when treated with phosphorus tri- or oxy-halide yield as primary products acid

The Thermal Decomposition of Quaternary Phosphonium Hydroxides.[1]

Trimethylethylphosponium hydroxide, $(CH_3)_3(C_2H_5)POH$, is obtained in the usual manner from the corresponding iodide. The latter is converted by sodium picrate into *trimethylethylphosphonium picrate*, separating from water in long needles, M.pt. 290° C. Thermal decomposition of the hydroxide gives an 88 per cent. yield of methane calculated on the iodide, and *dimethylethylphosphine oxide*, B.pt. 223° to 225° C., M.pt. 73° to 75° C., is obtained as a very hygroscopic compound, which gives an oily salt with trichloroacetic acid ; it also appears that there is a definite but minor side-reaction (< 5 per cent.) in which hydrogen is formed.

Methyltriethylphosphonium hydroxide, $(CH_3)(C_2H_5)_3POH$, decomposes when heated, giving about an 89 per cent. yield of methane calculated on the original iodide, and *triethylphosphine oxide*, B.pt. 238° to 240° C., M.pt. about 46° C., the corresponding *chromate* melting at 99° to 100° C. *Methyltriethylphosphonium picrate* separates from alcohol in prisms, M.pt. 239° C.

Triethyl - n - propylphosphonium hydroxide, $(C_2H_5)_3(C_3H_7)POH$.—The corresponding *iodide* is prepared by allowing *n*-propyl iodide and triethylphosphine in absolute alcohol to stand overnight at 30° C., the compound then being precipitated by ether and recrystallised from alcohol, from which it separates in colourless needles. The *picrate*, obtained from the iodide, is deposited from alcohol in rosettes of foliated needles, M.pt. 91° C. The hydroxide, also formed from the iodide, undergoes thermal decomposition, giving a 90 per cent. yield of hydrocarbons calculated on the iodide used, and phosphine oxides, B.pt. 245° to 247° C., M.pt. about 37° C. The hydrocarbons do not contain olefins and no phosphines are isolated.

Tri - n - propylethylphosphonium hydroxide, $(C_3H_7)_3(C_2H_5)POH$.—When tri-*n*-propylphosphine and ethyl iodide react at the ordinary temperature, they yield *tri-n-propylethylphosphonium iodide*, which separates from alcohol-ethyl acetate in needles, and may be converted to the *picrate*, crystallising in needles from benzene-ligroin, M.pt. 64° C. Distillation of the hydroxide gives a 90 per cent. yield of hydrocarbons calculated on the iodide and a mixture of phosphine oxides, B.pt. 253° to 257° C.

Tri - n - propyl - n - butylphosphonium hydroxide, $(C_3H_7)_3(C_4H_9)POH$.—The corresponding *iodide* separates from ethyl acetate as needles, M.pt. 239° to 240° C., and yields a *picrate*, consisting of small prisms from dilute acetic acid, M.pt. 67° C. Decomposition of the hydroxide yields phosphine oxides and an 85 per cent. yield of hydrocarbons calculated on the iodide used.

halides in which the hydroxyl group is intact. Hydrolysis of these products with water gives phosphorus derivatives of the free hydroxy-acids, which may be converted into salts of the alkaline earth metals. *Ricinstearolic acid* and *ricinolic acid* when treated with phosphorus trichloride or tribromide yield *compounds* $C_{18}H_{33}O_5P$ and $C_{18}H_{35}O_5P$ respectively.

Phosphorus derivatives of unsaturated higher fatty acids are dealt with in German Patents 257641, 271158, 271159 and 273219. These patents deal with *compounds* from *stearolic* and *behenolic acids* and their derivatives. The derivatives are probably of similar type to the products obtained in the arsenic series (see this Vol., Part II, p. 60).

[1] Fenton and Ingold, *J. Chem. Soc.*, 1929, p. 2342.

Tri - n - propyl - n - octylphosphonium hydroxide, $(C_3H_7)_3(C_8H_{17})POH$, is obtained from the corresponding *bromide*, which is the condensation product of tri-*n*-propylphosphine and *n*-octyl bromide. The liquid bromide may be converted to the *iodide* by means of sodium iodide in alcohol, or into the *chloride* through the hydroxide, but these salts are also liquids. The *chloroaurate* separates from alcohol in prisms, M.pt. 38° C. Distillation of the hydroxide gives a 19·8 per cent. yield of octane and a 66·2 per cent. yield of propane.

Tri - n - butyl - n - propylphosphonium hydroxide, $(C_4H_9)_3(C_3H_7)POH$, on distillation yields phosphine oxides and a gas which corresponds to propane, 26 vols. per cent., and butane, 74 vols. per cent.

Trimethylphenylphosphonium hydroxide, $(CH_3)_3(C_6H_5)POH$. —The *iodide* used in the preparation of this hydroxide melts at 236° C. The *picrate* separates from water in yellow needles, M.pt. 132° to 133° C.[1] The hydroxide decomposes on distillation, giving benzene and trimethylphosphine oxide. Nitration of the picrate at 60° C. with equal volumes of fuming nitric and sulphuric acids yields *m-nitrophenyltrimethylphosphonium picrate*, M.pt. 166° to 167° C.

Trimethylbenzylphosphonium hydroxide, $(CH_3)_3(C_7H_7)POH$. —The corresponding *bromide* separates from alcohol-ligroin in needles, M.pt. 222° C., and the *picrate* forms prisms, M.pt. 173° C. Thermal decomposition of the hydroxide yields trimethylphosphine oxide and toluene. Nitration of the picrate yields *p-nitrobenzyltrimethylphosphonium picrate*, consisting of needles, M.pt. 188° to 189° C.; the corresponding *ortho-* and *meta*-compounds are prepared from trimethylphosphine and *o-* or *m*-nitrobenzyl chloride, the *o-nitro-derivative* forming small needles, M.pt. 152° to 153° C., and the *m-nitro-compound* giving needles, M.pt. 171° to 172° C.

Triphenylbenzylphosphonium hydroxide, $(C_6H_5)_3(C_7H_7)POH$. —The corresponding *bromide* crystallises from water or alcohol-ethyl acetate in needles, M.pt. 288° C. Thermal decomposition of the hydroxide gives a 100 per cent. yield of triphenylphosphine oxide (pure product M.pt. 154° to 156° C.) and a 70 per cent. yield of toluene.

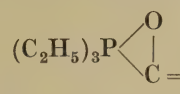
Triethyl-β-phenylethylphosphonium hydroxide, $(C_2H_5)_3(C_6H_5.C_2H_4)POH$.—The corresponding *chloride* is a syrup, and the *picrate* separates from chloroform-ligroin in prisms, M.pt. 70° C. Distillation of the hydroxide yields ethylbenzene (84·1 per cent.), styrene (4·5 per cent.), ethane (6·6 per cent.) and triethylphosphine oxide.

Tri - n - butyl - $\beta\beta$ - diphenylethylphosphonium hydroxide, $(C_4H_9)_3[(C_6H_5)_2C_2H_3]POH$, when distilled, gives tri-*n*-butylphosphine, *asym.*-diphenylethylene, 10 per cent. of *asym.*-diphenylethane, and a small quantity of a viscous syrup, probably tri-*n*-butylphosphine oxide.

ω - Carbethoxytrimethylphosphonium hydroxide, $(CH_3)_3(C_2H_5CO_2)POH$.—The corresponding *chloride*, from trimethylphosphine and ethyl chloroacetate, forms hygroscopic needles, melting with decomposition at 160° C. The *picrate* separates from alcohol in rhombs, M.pt. 124° to 125° C. Distillation of the hydroxide gives trimethylphosphine oxide and small quantities of alcohol, the identification of other products not appearing to have been very satisfactory.

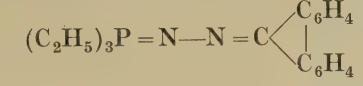
[1] Compare Ingold, Shaw and Wilson, *J. Chem. Soc.*, 1928, p. 1280.

Phosphazines, Phosphenemethylene Derivatives and Phosphinimines.



The above compound is obtained by the combination of diphenylketen with triethylphosphine in absolute ether, the body immediately being precipitated as a faint yellow hygroscopic mass. The crystals are stable in dry ether, but with water triethylphosphine and diphenylacetic acid are formed. The compound sinters at about 80° C. and is completely decomposed at 100° C.; heating in a test-tube drives off triethylphosphine, and orange-coloured diphenylketen remains. In ether or petroleum ether the body is insoluble, but in benzene an orange-yellow solution is obtained, showing dissociation; addition of aniline to the solution gives diphenylacetanilide.

Triethylphosphine fluorenone azine,[2]



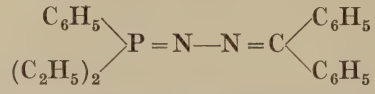
To a solution of 18·6 grams of diazofluorene in 120 c.c. of benzene, in a nitrogen atmosphere and with ice cooling, 11·2 grams of triethylphosphine diluted with 20 c.c. of benzene are slowly added. Heat is evolved and after ten minutes thick yellow crystals separate, which, after 1½ hours, are removed and washed with ether (yield, 19·1 grams). The phosphazine thus obtained melts at 154° to 158° C., and is very sensitive to moisture, so that it cannot be recrystallised from moist solvents. Rapid crystallisation from hot benzene gives golden-yellow crystals, M.pt. 160° C. When heated above its melting-point the compound decomposes with evolution of nitrogen. It forms a basic *addition product* with *methyl iodide*, a faintly yellow powder, M.pt. 109° to 113° C. Dilute hydrochloric and sulphuric acids dissolve the phosphazine unchanged, but heating with concentrated acid decomposes it, as also does the prolonged action of cold concentrated acid. Hydrogen chloride gives a yellow *hydrochloride* which decomposes in moist air. The phosphazine is soluble in carbon disulphide, the solution being dark blue-violet. Short boiling with alcohol gives fluorenone hydrazine; if this is removed and the mother liquor evaporated, a residue of triethylphosphine oxide remains. By the action of chloroform-alcohol mixture on the phosphazine, a compound containing no phosphorus is obtained, probably bi-diphenylenetetrahydrotetrazine,

Triethylphosphine benzophenone azine, $(C_2H_5)_3P=N—N=C(C_6H_5)_2$, is obtained by the interaction of diphenyldiazomethane and triethylphosphine in petroleum ether, employing a carbon dioxide atmosphere and cooling, the phosphazine soon separating in yellow

[1] Staudinger and Meyer, *Helv. Chim. Acta*, 1919, 2, 612.
[2] *Ibid.*, p. 619.

crystals. The body is not very stable and decomposes if allowed to stand for an hour, bi-diphenyltetrahydrotetrazine being formed.

Phenyldiethylphosphine benzophenone azine,



is obtained from diphenyldiazomethane and diethylphenylphosphine in ether. It forms faintly yellow crystals, M.pt. 113° C., which begin to evolve nitrogen at 160° C. When boiled for one hour with dilute alcohol the body is hydrolysed to benzophenone hydrazone, and from the evaporated mother liquor diethylphenylphosphine oxide is obtained. Dilute and concentrated hydrochloric acid solutions of the phosphazine are colourless; concentrated sulphuric acid solutions are yellow, changing to colourless on dilution.

Triphenylphosphine benzophenone azine $(C_6H_5)_3P=N—N=C(C_6H_5)_2$, is prepared from triphenylphosphine and diphenyldiazomethane in petroleum ether-ether mixture. The yield is about 88 per cent. and the product is a white, crystalline powder, melting with decomposition at 173° C., readily soluble in chloroform or benzene, sparingly soluble in ether or light petroleum. The compound remains stable after keeping for several weeks. Prolonged boiling with alcohol converts it into triphenylphosphine oxide and benzophenone hydrazone. The azine is sparingly soluble in dilute hydrochloric and sulphuric acids; in concentrated sulphuric acid it dissolves readily, giving a yellow solution, from which it is precipitated unchanged on the addition of water. Hydrogen chloride yields a *hydrochloride*, a white, crystalline powder, decomposing at about 180° C. and containing about 2 molecules of hydrochloric acid; it is only sparingly soluble in benzene.

Triphenylphosphine glyoxyl ester azine, $(C_6H_5)_3P=N—N=CH.CO_2C_2H_5$, occurs when triphenylphosphine and diazoacetic ester in ether solution are allowed to stand for a month. It crystallises from ether-benzene solution in white crystals, M.pt. 113° to 114° C.[1]

Triphenylphosphine fluorenone azine, $(C_6H_5)_3P=N—N=C(C_6H_4)_2$, is the condensation product of triphenylphosphine and diazofluorene, but the action is much slower than with triethylphosphine. The product forms golden-yellow crystals, M.pt. 204° to 205° C. It may be kept for a month without decomposing, and may be recrystallised from alcohol without hydrolysis. On recrystallisation it yields yellow, compact crystals, M.pt. 209° to 210° C. When heated to 220° C. it suddenly evolves nitrogen. It is a much feebler base than the triethylphosphine derivative and it does not add on methyl iodide. It dissolves in dilute or concentrated hydrochloric acid, is insoluble in dilute sulphuric acid, but in concentrated sulphuric acid yields an orange-red solution, which, on dilution with water, deposits the base unchanged. It resembles the triethylphosphine derivative in forming an *addition product* with 2 molecules of *hydrochloric acid*.

Phenyldiethylphosphine fluorenone azine, $(C_6H_5)(C_2H_5)_2P=N—N=C(C_6H_4)_2$, obtained from phenyldiethylphosphine and diazofluorene, is a yellow, crystalline product, melting at 115° C., and losing nitrogen at 220° to 270° C. It is fairly stable and can be recrystallised

[1] The products obtained from triethylphosphine and phenyldiethylphosphine with diazoacetic ester have not been analysed.

from benzene or chloroform, but is only sparingly soluble in ether or petroleum ether. After keeping for 5 weeks the compound decomposes. It is hydrolysed by aqueous alcohol on heating on the water-bath, yielding fluorene hydrazone and phenyldiethylphosphine oxide. The azine possesses feeble basic properties, is slightly soluble in dilute hydrochloric and sulphuric acids, dissolves in concentrated hydrochloric acid to give a yellow solution, and in concentrated sulphuric acid yielding a scarlet solution which becomes colourless on dilution.

Triphenylphosphine diphenylmethylene, $(C_6H_5)_3P=C(C_6H_5)_2$,[1] is the decomposition product of triphenylphosphine benzophenone azine when the latter is heated in an oil-bath in an atmosphere of nitrogen for 15 minutes at 185° to 195° C. It is decomposed by water or alcohol, but separates from benzene in garnet-red plates containing about 2 molecules of benzene. The latter is difficult to remove, even by heating *in vacuo* at 40° to 50° C. The pure product melts to a deep red liquid at 170° to 172° C. When heated with dilute hydrochloric acid it gives a colourless solution, from which the *hydrochloride* of *triphenylbenzhydrylphosphonium hydroxide* separates as white needles on cooling, M.pt. 240° to 242° C. Triphenylphosphine diphenylmethylene reacts with carbon disulphide[2] on heating for 16 hours at 60° C.; triphenylphosphine sulphide separates on cooling, and the mother liquor, after removing the solvent and treating with acetic acid, gives a further quantity of the sulphide, polymerised keten and a yellow amorphous product.

Triphenylphosphine phenylimine, $(C_6H_5)_3P=NC_6H_5$.[3]—This occurs when triphenylphosphine condenses with phenyl azide in ether solution. The reaction is very violent and a vigorous evolution of nitrogen takes place, the product separating out as a white powder, M.pt. 131° to 132° C. after crystallisation from ether. By slow crystallisation, plates are obtained, readily soluble in benzene, sparingly soluble in petroleum ether. The compound shows feeble basic properties, being somewhat soluble in dilute hydrochloric or sulphuric acid, and when boiled is hydrolysed to triphenylphosphine oxide and aniline. Cold concentrated sulphuric acid dissolves the compound, and dilution of the solution with water precipitates triphenylphosphine oxide, aniline sulphate remaining in solution. Boiling for a short time with carbon disulphide gives triphenylphosphine sulphide, M.pt. 156° to 158° C., and phenylthiocarbimide. Triphenylphosphine oxide and sulphide are similarly obtained when the compound is gently warmed with phenylcarbimide or phenylthiocarbimide, respectively.

Triphenylphosphine-p-tolylimine, $(C_6H_5)_3P=N.C_6H_4.CH_3$, is isolated from triphenylphosphine and *p*-tolyl azide in 93 per cent. yield. It forms faintly yellow crystals from ether, M.pt. 134° to 135° C. If carbon dioxide be passed into the molten compound, triphenylphosphine oxide and *p*-tolyl*iso*cyanate result, and with carbon disulphide, triphenylphosphine sulphide and *p*-tolylthiocarbimide are obtained.

Triphenylphosphine-m-xylylimine, $(C_6H_5)_3P=N.C_6H_3(CH_3)_2$, occurs in 85 per cent. yield when *m*-xylyl azide is used in the foregoing reaction. The product melts at 130° to 131° C. and gives similar

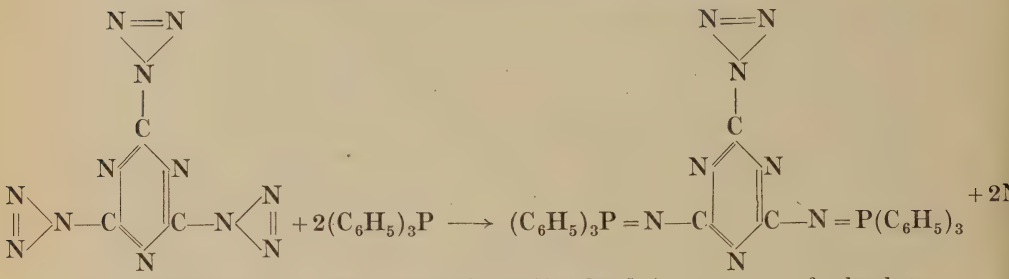
[1] Staudinger and Meyer, *loc. cit.*, 1919, 635.
[2] Staudinger, Rathsam and Kjelsberg, *loc. cit.*, 1920, 3, 853.
[3] Staudinger and Meyer, *loc. cit.*

results with carbon dioxide and carbon disulphide as the preceding derivative.

Phosphorus trichloride and phenyldichlorophosphine do not react with phenyl azide.

Cyanurphosphinimines.[1]

Cyanurdi-triphenylphosphinimine monoazide,

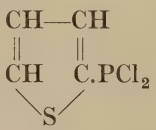


Triphenylphosphine (7·5 grams) is dissolved in 40 c.c. of absolute alcohol and to the solution 2·7 grams of cyanurtriazide in 100 c.c. of absolute ether are added in small portions. After a time the solution becomes intense green in colour and nitrogen is evolved. A white crystalline powder separates and the reaction is completed by warming for a short time under reflux. The product is filtered off and well washed with ether to remove any unchanged starting materials. The yield is practically theoretical and the product is a light, odourless powder, melting with decomposition at 243° C. It dissolves readily in acetone or benzene, is sparingly soluble in hot alcohol and insoluble in ether.

Cyanurtri-triphenylphosphinimine.—3 grams of the preceding compound and 2 grams of triphenylphosphine are mixed together and heated in an oil-bath to 180° C. The mixture melts and nitrogen is evolved, a pale brown mass resulting. This is triturated with ether and washed with the same solvent. The resulting product crystallises from xylene in white needles, M.pt. 239° C., soluble in hot alcohol, acetone, benzene or xylene, insoluble in ether.[2]

Phosphorus Derivatives of Thiophene.[3]

Thienyldichlorophosphine,



is obtained only in small yield when thiophene reacts with phosphorus trichloride in the presence of aluminium chloride. When the mixed vapours of thiophene and phosphorus trichloride are passed for 8 days

[1] Kesting, *J. prakt. Chem.*, 1923, (2), 105, 242.

[2] Compare the following reaction (Staudinger and Meyer, *Helv. Chim. Acta*, 1919, 2, 635; *Ber.*, 1921, 54, 179):

$$C_6H_5N_3 + (C_6H_5)_3P \longrightarrow C_6H_5N{=}N{-}N{=}P(C_6H_5)_3 \longrightarrow C_6H_5N{=}P(C_6H_5)_3 + N_2$$

[3] Sachs, *Ber.*, 1892, 25, 1514.

over pumice heated to dull redness, only 14 grams of the dichlorophosphine result from 100 grams of thiophene, 60 grams of the latter being recovered. The product boils at 218° C. and is decomposed by water to the phosphinous acid. Treatment with chlorine yields a *tetrachloride*, decomposed by water to the *oxychloride* and finally the phosphinic acid. The oxychloride, $C_4H_3S.POCl_2$, is best obtained by treating the tetrachloride with sulphur dioxide; it boils at 258° to 260° C.

Thienylphosphinous acid, $C_4H_3S.P(OH)_2$, prepared as stated in the foregoing, forms needles, M.pt. 70° C., and has similar properties to the corresponding phenyl compound.

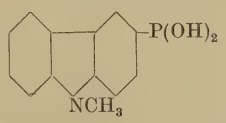
Thienylphosphinic acid, $C_4H_3S.PO(OH)_2$, obtained from the tetrachloride and water, separates from the latter solvent as short needles, M.pt. 159° C., readily soluble in water or alcohol, less soluble in ether, insoluble in benzene. The *normal silver salt* is a white powder, soluble in ammonium hydroxide and nitric acid.

Thienyldiethylphosphine, $C_4H_3S.P(C_2H_5)_2$, is formed by the condensation of zinc diethyl and thienyldichlorophosphine in ether solution. It is a pale yellow, pungent liquid, B.pt. 225° C. With methyl iodide it gives *thienyldiethylmethylphosphonium iodide*, a white powder, M.pt. 122° C., readily soluble in water or alcohol, insoluble in ether. The corresponding *phosphonium chloride* gives a *platinichloride*, a yellow crystalline powder. *Thienyltriethylphosphonium iodide* has been isolated, but the reaction by which it is prepared is not so violent as with methyl iodide.

Phosphorus Compounds of the Carbazole Series.[1]

9-Alkyl (or benzoyl)-carbazole phosphinous acids are formed when phosphorus trichloride reacts with 9-alkyl (or benzoyl)-carbazoles.

9-Methylcarbazole-3-phosphinous acid,



9-Methylcarbazole is heated at 150° C. and slowly treated with phosphorus trichloride. After cooling, the melt is added to a mixture of sodium hydroxide (density 1·36) and ice. The whole is extracted with ether, concentrated, and the phosphinous acid precipitated by the addition of acid. The resulting carbazole derivative is very resistant to acids. 9-*Ethylcarbazole*-3-*phosphinous acid* is obtained by a similar process.

The Interaction of Benzophenone and Hypophosphorous Acid.[2]

When benzophenone and hypophosphorous acid are heated together for some days, a homogeneous mixture is obtained. The mass is extracted with hot water, the addition of lead acetate to the solution precipitating the *lead salt* of an acid of the formula $HO.C(C_6H_5)_2.P(OH)_2$. This salt is insoluble in water, but dissolves in acetone, alcohol or ether. The *free acid*, obtained by decomposition of the lead

[1] British Patent, 258744 (1925).

[2] Marie, *Compt. rend.*, 1903, 136, 508.

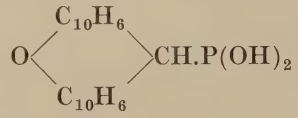
salt with hydrogen sulphide, crystallises from water in thin plates, M.pt. 150° to 151° C. It is soluble in all common solvents except ether, is stable towards alkalis and may be boiled with hydrochloric acid without decomposition. Oxidation with bromine gives an *acid* of composition $HO.C(C_6H_5)_2.PO(OH)_2$, M.pt. 184° to 185° C., which is dibasic, and yields insoluble *silver* and *barium salts*.

The Interaction of Aromatic Alcohols and Hypophosphorous Acid.[1]

Triphenylmethylphosphinous acid, $(C_6H_5)_3C.P(OH)_2$, is formed when triphenylcarbinol is heated with hypophosphorous acid and the yellow product boiled with sodium hydroxide. The acid melts at 94° C. An oily residue of triphenylmethane remains and a little triphenylcarbinol is recovered. When the reaction is carried out with sodium hypophosphite in the presence of acetic acid and sulphuric acid, the carbinol is almost completely converted into the acid, whilst the presence of acetic acid alone gives an almost quantitative yield of the hydrocarbon.

Tetramethyldiaminobenzhydrylphosphinous acid, $CH[C_6H_4.N(CH_3)_2]_2.P(OH)_2$, is obtained together with the corresponding hydrocarbon when hypophosphorous acid reacts with " Michler's hydrol." The acid yields colourless crystals, M.pt. 90° C., and reduces alcoholic silver nitrate on boiling.

In a similar manner dinaphthapyranol forms dinaphthapyran and *dinaphthapyrylphosphinous acid* :



No further details of this product have been given.

Indolylphosphines.[2]

The indolylphosphines are colourless and odourless. The 2- and 3-indolyl compounds yield N-silver derivatives, soluble in ammonium hydroxide, and are unaffected by boiling concentrated alkali hydroxide. The 1-indolyl compounds, on the other hand, form no silver derivatives and yield phosphine on treating with moist solvents or boiling with water.

Tri-3-indolylphosphine, $(C_8H_6N)_3P$.—Indole, magnesium and ethyl bromide are caused to react, when magnesium indole results. This substance reacts with phosphorus trichloride in ether to give tri-3-indolylphosphine, M.pt. 195° to 196° C., and a small quantity of *tri-1-indolylphosphine*, M.pt. 223° to 225° C. The separation of these two derivatives is effected by treatment with acetone.

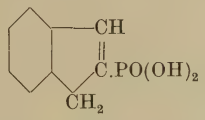
Tri-2-methyl-1-indolylphosphine, $(C_9H_8N)_3P$, is produced by the interaction of magnesium 2-methylindole and phosphorus trichloride. It melts at 180° C. If magnesium 3-methylindole is used in the condensation, *tri-3-methyl-2-indolylphosphine*, M.pt. 156° to 158° C., results, and from it a *methiodide* is obtained, M.pt. 171° C.

[1] Fosse, *Compt. rend.*, 1910, **150**, 178; *Bull. Soc. chim.*, 1910, [iv], **7**, 228, 231.
[2] Mingoia, *Gazzetta*, 1930, **60**, 144.

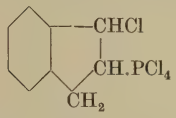
Phosphinic Acids from some Unsaturated Derivatives.[1]

One of the chlorine atoms in phosphorus pentachloride appears to hold a unique position in that the products of the reaction with indene, styrene, α-methylstyrene and *asym.*-diphenylethylene in cold benzene solution, suffer hydrolysis accompanied by intramolecular separation of the fifth chlorine atom as hydrogen chloride when treated with water. At much higher temperatures certain indones add on two chlorine atoms when treated with phosphorus pentachloride, this decisively indicating the fission $PCl_5 = PCl_3 + Cl_2$.

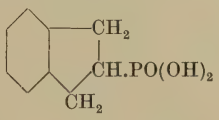
Indenyl-2-phosphinic acid,



Finely powdered phosphorus pentachloride (105 grams) is suspended in 250 c.c. of dry benzene and 29 grams of indene added dropwise, moisture being excluded during the operation. A little hydrogen chloride is evolved, and after standing overnight, the colourless reaction mixture is poured into a large volume of water. A violent hissing results, accompanied by a sluggish evolution of hydrogen chloride; complete solution is attained and in time the required acid separates. After several hours this is removed and dried, about 32 grams of crude product resulting. Crystallisation from 100 c.c. of acetic acid gives 25 grams of white crystals, M.pt. 184° C., turning deep red at 200° C., probably owing to oxidation to *indone-2-phosphinic acid.* The acid is monobasic towards methyl orange and dibasic towards phenolphthalein. The *silver hydrogen*, *lead*, *mercurous*, *thallous*, *copper*, *mercuric*, *cadmium*, *nickel*, *ferric*, *ferrous*, *aluminium*, *barium* and *calcium salts* are known. The acid is stable towards bromine, but the presence of the ethylenic linking is established by its conversion to hydrindyl-2-phosphinic acid. In the foregoing preparation the compound formed by the interaction of indene and phosphorus pentachloride, prior to the action of water, probably has the constitution



Hydrindyl-2-phosphinic acid,

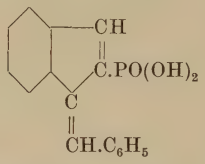


A solution of 2 grams of indenyl-2-phosphinic acid in 25 c.c. of propyl alcohol is boiled for two hours with one gram of palladised barium sulphate, a stream of hydrogen being passed through the solution during the operation. After filtration, the solution is evaporated *in vacuo* at 50° C., and the residue crystallised from acetic acid and washed with methyl alcohol. About 0·6 gram of white prisms is obtained,

[1] Bergmann and Bondi, *Ber.*, 1930, 63, [B], 1158.

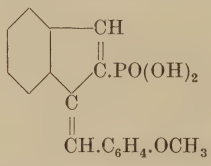
M.pt. 196° C. to a colourless liquid, the product yielding a water-insoluble *silver salt.*

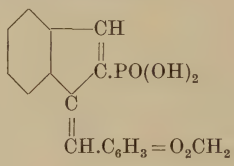
1-Benzylidene indenyl-2-phosphinic acid,



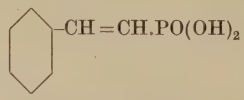
Four grams of indenyl-2-phosphinic acid in 30 c.c. of absolute alcohol, 1·4 grams of sodium in 40 c.c. of absolute alcohol, and 2·1 grams of benzaldehyde in the same solvent, are shaken together on a machine for three days. The yellow product is removed, washed with a little alcohol and dissolved in hot water. After filtration the solution is acidified with hot dilute sulphuric acid and placed in an ice-chest for twelve hours. The yellow needles which separate (2 grams) are washed with a little ice-cold water, the product melting at 188° to 189° C. and becoming red. The acid yields *silver*, *lead* and *ferric salts.*

In a similar manner *1-anisylideneindenyl-2-phosphinic acid*, M.pt. 192° C., and *1-piperonylideneindenyl-2-phosphinic acid*, M.pt. 194° C., are isolated as yellow needles showing decomposition on melting. The formulæ of these two compounds are as follows :—



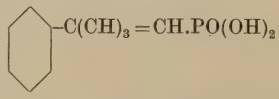


Styryl-β-phosphinic acid,



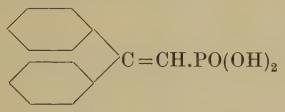
is obtained from styrene and phosphorus pentachloride in benzene solution in a similar manner to indenyl-2-phosphinic acid. It forms white needles, M.pt. 146° C., and there are indications of *cis-trans* isomerides being formed. The *silver*, *lead*, *mercurous*, *thallous*, *ferrous*, *ferric*, *copper*, *nickel*, *barium* and *calcium salts* are known. Hydrogenation of the acid yields phenylethylphosphinic acid, M.pt. 137° to 138° C.

α-Methylstyryl-β-phosphinic acid,



prepared by condensing α-methylstyrene with phosphorus pentachloride and treating the resulting product with water, melts at 95° C., and yields *silver*, *lead*, *mercurous*, *ferrous*, *ferric*, *nickel*, *barium* and *calcium salts.* The corresponding hydrogenated acid is an oil. Oxidation of α-methylstyryl-β-phosphinic acid by chromic acid affords acetophenone.

$\beta\beta$-Diphenylvinylphosphinic acid,



is prepared from the interaction of *asym.*-diphenylethylene and phosphorus pentachloride in dry benzene, followed by treatment with water. It forms white crystals, M.pt. 167° C., and gives *silver*, *lead*, *mercury*, *copper*, *nickel*, *ferrous*, *ferric*, *barium* and *calcium salts*. The acid can be hydrogenated to *$\beta\beta$-diphenylethane-d-phosphinic acid*, M.pt. 213° C., and oxidised to benzophenone.

Phosphorus-Arsenic Derivatives.

Arseno-phosphorus compounds have been obtained by treating *m*-amino-*p*-hydroxyphenylarsinic acid with phosphoryl chloride in the presence of aqueous sodium hydroxide and subsequently reducing the mixture with sodium hydrosulphite. The compounds are soluble in dilute sodium carbonate and in hydrochloric acid, their alkaline solutions reducing Fehling's solution and Nessler's and Tollen's reagents.[1]

For the determination of phosphorus in organic compounds, see Hofmann, *Ber.*, 1872, 5, 104; Monthulé, *Ann. Chim. anal.*, 1904, 9, 308; Pringsheim, *Amer. Chem. J.*, 1904, 31, 386; *Ber.*, 1904, 37, 2155. For the determination of carbon and hydrogen in organometallic phosphorus compounds, see Londner, *Ber.*, 1922, 55, [B], 2025; *Zeitsch. anal. Chem.*, 1925, 66, 305.

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[1] English Patent, 9234 (1915); German Patent, 269700.

CHAPTER IV.

ALIPHATIC COMPOUNDS OF ANTIMONY.

Compounds of the Type R_3Sb.

The tertiary alkyl stibines may be produced in a variety of ways :

(1) The most important method consists of treating magnesium alkyl halides with antimony trihalides.

$$3RMgX + SbX_3 = R_3Sb + 3MgX_2$$

This reaction is always accompanied by the separation of finely divided antimony, and when alkyl stibines are mixed with antimony trichloride there is always immediate reduction to antimony.

(2) An alloy of antimony and potassium is mixed with sand and treated with an alkyl iodide :

$$K_3Sb + 3RI = R_3Sb + 3KI$$

(3) By the interaction of zinc dialkyls and antimony trihalides :

$$3R_2Zn + 2SbX_3 = 2R_3Sb + 3ZnX_2$$

(4) The zinc dialkyls in (3) may be replaced by mercury dialkyls :

$$3R_2Hg + 2SbX_3 = 2R_3Sb + 3HgX_2$$

(5) By treating trialkylstibine dihalides with zinc :

$$R_3SbX_2 + Zn = R_3Sb + ZnX_2$$

(6) By heating quaternary alkyl stibonium iodides with potassium-antimony alloy in the presence of carbon dioxide :

$$3R_4SbI + K_3Sb = 4R_3Sb + 3KI$$

The quaternary stibonium compounds are formed in reaction (2) and have subsequently to be dealt with according to equation (6).

All the trialkylstibines are clear liquids, having a peculiar odour, and owing to the ease with which they oxidise, special apparatus has been devised for their preparation. The lower members may be distilled under reduced pressure, but tri-*n*-hexylstibine is partly decomposed under these conditions. The density of the compounds shows a regular fall as the series is ascended and the boiling-points rise. The compounds are only slightly soluble in water or aqueous alcohol, but dissolve in alcohol, ether or carbon disulphide. With the latter solvent they do

not yield coloured compounds like the corresponding phosphines, and they only combine slowly with alkyl iodides. Trialkylstibines readily combine with oxygen with evolution of heat, the clear liquid immediately becoming turbid, but as the molecular weight increases the ease of oxidation diminishes. Stibines ignite when warmed in air, with formation of antimonious oxide. Chlorine, bromine, iodine, cyanogen bromide and iodide, sulphur and selenium, readily combine with the stibines forming addition products in which the antimony becomes pentavalent, R_3SbX_2. Trimethylstibine forms a large number of double salts with platinum and palladium chlorides. The stibines reduce mercuric salts to the metal in the cold, and a similar reduction takes place with auric and silver salts on warming.

Trialkylstibine Oxides.—Six stibine oxides are known: the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl and *iso*amyl derivatives. The first two are obtained by treating the corresponding sulphate with barium hydroxide or by regulated atmospheric oxidation of the stibine; the remainder are formed by the latter process. Oxidation of the stibines may also be brought about by treating their solutions in alcohol with finely divided mercuric oxide. The methyl, ethyl and *iso*amyl oxides are solids, and the compounds show a decreasing solubility in water with rise of molecular weight; they exhibit decidedly more basic properties than the corresponding arsenical compounds. The methyl derivative forms a double compound with the dichloride, $(CH_3)_3SbO.(CH_3)_3SbCl_2$.

Trialkylstibine Sulphides and Selenides.—Only the methyl and ethyl compounds are known with certainty, and these may be obtained as follows:—

(1) An ether solution of the stibine is heated with sulphur or selenium:

$$R_3Sb + S = R_3SbS$$
$$R_3Sb + Se = R_3SbSe$$

(2) An aqueous solution of the trialkylstibine oxide is treated with hydrogen sulphide:

$$R_3SbO + H_2S = R_3SbS + H_2O$$

(3) Trialkylstibine dibromide is allowed to react with potassium ethylate and the product treated with hydrogen sulphide:

$$R_3SbBr_2 + 2KOC_2H_5 = R_3Sb(OC_2H_5)_2 + 2KBr$$
$$R_3Sb(OC_2H_5)_2 + H_2S = R_3SbS + 2C_2H_5OH$$

The intermediate ethoxide is not isolated in this process.

The sulphides are crystalline products, which melt with decomposition. Triethylstibine selenide is the only representative of its class, and it soon decomposes with separation of selenium.

Trialkylstibine Dihalides, Hydroxyhalides and Cyanohalides.—The dihalides may be isolated in several ways. The stibines combine directly with the halogens to give dihalides, but this method needs regulation, as some of the trialkylstibines of low molecular weight combine explosively with the halogens. Chlorine has also been coupled to the antimony by heating the stibine in a sealed tube with hydrochloric acid. The latter is also capable of converting trialkylstibine oxides

or dinitrates to dichlorides. Antimony combines directly with alkyl iodides at about 140° C. to give trialkylstibine di-iodides; mercuric bromide or chloride can transform such di-iodides to dibromides or dichlorides. Magnesium ethyl iodide and antimony pentachloride react to form triethylstibine dichloride, and a double compound of trimethylstibine dichloride and methylmercuric chloride results when mercury dimethyl reacts with antimony trichloride. Hydroxyhalides are known only in the methyl series, the hydroxybromide being prepared by hydrolysis of the cyanobromide, this method of preparation being analogous to that used for the corresponding arsenical compounds :

$$R_3Sb.CN.Br + H_2O = R_3Sb.OH.Br + HCN$$

The colourless trimethylstibine di-iodide appears to be most suitably represented by the formula $I^-[Sb(CH_3)_3]^{++}I^-$, *i.e.* as a completely ionised, tertiary electrolyte. This assumption is based on the fact that the compound does not exhibit an absorption band in the ultra-violet region.[1] The molecular conductivities of the dihalides when determined in acetonitrile indicate that the compounds are weak electrolytes only if their hydrolysis is prevented by the absence of water. The hydroxychloride is represented by the formula $[Sb(CH_3)_3(OH)]^+Cl^-$, hydrogen chloride being liberated when a very large excess of water is present. Since its solution has an acid reaction, the hydroxychloride possesses only a slight tendency to eliminate hydroxyl ions. The colourless base is a very weak electrolyte, although both hydroxyl groups can be replaced if sufficient acid is added to precipitate the dihalide.

Trimethylstibine, $(CH_3)_3Sb$, may be prepared as follows : (1) The Grignard solution from 35·5 grams of methyl iodide and 6·1 grams of magnesium in 200 to 300 c.c. of dry ether is treated dropwise with a solution of 18·9 grams of antimony trichloride in 80 to 100 c.c. of ether. The reaction is very violent and when it is complete the flask is placed in an oil-bath and distillation carried out in a stream of carbon dioxide until the temperature reaches 170° C. The stibine distils over with the ether and is converted into its dibromide, from which it may be liberated as required. The yield of stibine is 60 to 70 per cent.[2] A convenient apparatus for obtaining the stibine from its dibromide is shown in fig. 1.[3] Weighed quantities of the dibromide are introduced into the flask A together with a small quantity of water and the calculated amount of finely granulated zinc (Kahlbaum No. 1). The air in the apparatus having previously been expelled by a stream of carbon dioxide, the mixture is distilled and the trimethylstibine collected in the graduated receiver B. The reaction vessel E is turned through an angle of 120° by means of the movable rubber joint J, so that the filter disk L is raised above the reacting liquids. A slight excess of aqueous platinic or palladous chloride solution is delivered into E from the tap funnel D, and to this is slowly added the calculated amount of trimethylstibine from the graduated receiver B. As the tertiary stibine is not miscible with aqueous solutions, the chemical combination is facilitated by shaking the vessel E, and when the reaction is completed the apparatus is rotated so that the attach-

[1] Lowry and Simons, *Ber.*, 1930, 63, [B], 1595.
[2] Hibbert, *Ber.*, 1906, 39, 160.
[3] Morgan and Yarsley, *Trans. Chem. Soc.*, 1925, 127, 184.

ments of the vessel E are in the vertical position, as shown in the diagram. By aspiration at K, the liquid contents of E are drawn through the filter L, on which the insoluble product is collected. The precipitate is now washed with ether introduced through the tap funnel C, and the ether washings are aspirated into the receiver F. Here the aqueous and ether filtrates are separated, the former being drawn off into the flask G, whilst the latter is collected in the distilling flask H, which is fitted with a condenser P. On distilling off the solvent, a residue is obtained of the ether-soluble product, which is shown to be trimethylstibine dichloride.

When alcoholic platinic chloride is employed the reaction is more vigorous because of the miscibility of trimethylstibine with this medium. The insoluble product is collected as before on the filter L, whilst the alcoholic filtrate and washings are drawn into the flask H. On removing the solvent, the residue contains trimethylstibine dichloride and *bis*trimethylstibine-dichloroplatinum (or palladium).

The whole apparatus is so designed that the platinous and palladous derivatives of the highly inflammable trimethylstibine can be prepared, collected and desiccated in an inert atmosphere and out of contact with air.

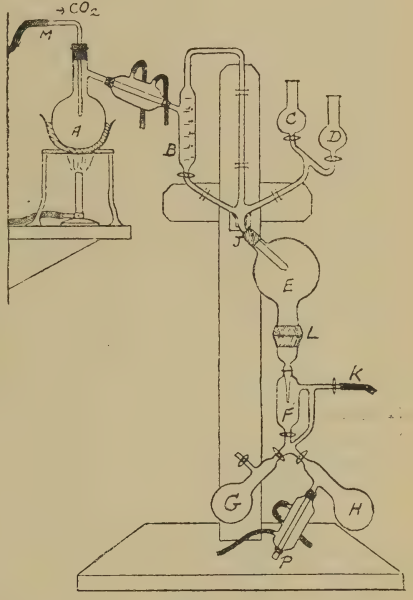


Fig. 1.

(2) Pure methyl iodide is slowly added to a mixture of an alloy of potassium and antimony and sand. The reaction is extremely violent and when it subsides the mixture is distilled in a carbon dioxide atmosphere, the stibine and methyl iodide combining to form tetramethylstibonium iodide. This is dried and distilled with potassium-antimony alloy in the presence of carbon dioxide, when pure trimethylstibine is obtained.[1]

Trimethylstibine is a transparent, colourless liquid, B.pt. 80·6° C. at 760 mm., density 1·523 at 15° C., and has an odour resembling that of onions. In water or dilute alcohol it is only very slightly soluble, but it dissolves readily in absolute alcohol, ether or carbon disulphide. It is readily oxidised in air, but inflames only when in large quantities. In chlorine gas it inflames. It combines directly with sulphur, cyanogen bromide [2] and cyanogen iodide at −20° C.[3] It reduces gold, silver and mercury salts to the free metals. Trimethylstibine reacts with platinic chloride to yield the compounds detailed overpage.[4]

[1] Landolt, *Annalen*, 1851, 78, 91; 1852, 84, 44; *J. prakt. Chem.*, 1861, 84, 329; *Jahresber.*, 1861, p. 569.

[2] Morgan and Yarsley, *Proc. Roy. Soc.*, 1925, 110, 534.

[3] Hantzsch and Hibbert, *Ber.*, 1907, 40, 1514.

[4] Morgan and Yarsley, *Trans. Chem. Soc.*, 1925, 127, 184.

The addition of trimethylstibine to aqueous platinic chloride in the air-free apparatus previously described gives an orange precipitate of *tetrakistrimethylstibine platinous platinochloride*, $[Pt.4(CH_3)_3Sb]PtCl_4$. This substance also results when a slight excess of aqueous potassium platinochloride is added to *tetrakis*trimethylstibine platinous chloride in water, or when *tetrakis*trimethylstibine platinous platinichloride is treated with a slight excess of aqueous chloroplatinic acid. Tetrakistrimethylstibine platinous platinochloride, when left for several months or rapidly heated at 65° C., undergoes depolymerisation to *bis*trimethylstibinedichloroplatinum. Both modifications occur when trimethylstibine and platinic chloride react in alcoholic solution; the orange dimeric compound is precipitated, whilst the monomeric derivative remains in solution. *Bistrimethylstibinedichloroplatinum*, $[2(CH_3)_3Sb.PtCl_2]$, crystallises from alcohol in pale yellow leaflets, and does not yield the "green salt of Magnus," $PtCl_2(NH_3)_2$, when treated with "Reiset's chloride," $[Pt.4NH_3]Cl_2$. When chlorine is passed through an alcoholic solution of the compound, trimethylstibine dichloride results; with hydroxylamine hydrochloride and sodium acetate complete reduction takes place, and with excess of pyridine, tetrapyridineplatinous chloride is formed. When *tetrakis*trimethylstibineplatinous platinochloride is treated with trimethylstibine and the resulting orange-brown crystals are allowed to interact with chloroplatinic acid in aqueous solution, a golden-yellow substance, *tetrakistrimethylstibineplatinous chloride*, $[Pt.4(CH_3)_3Sb]Cl_2$, is obtained. This reacts with aqueous palladous chloride to give *tetrakistrimethylstibineplatinous palladochloride*, $[Pt.4(CH_3)_3Sb]PdCl_4$, consisting of brown leaflets decomposing completely in 24 hours on exposure to the air.

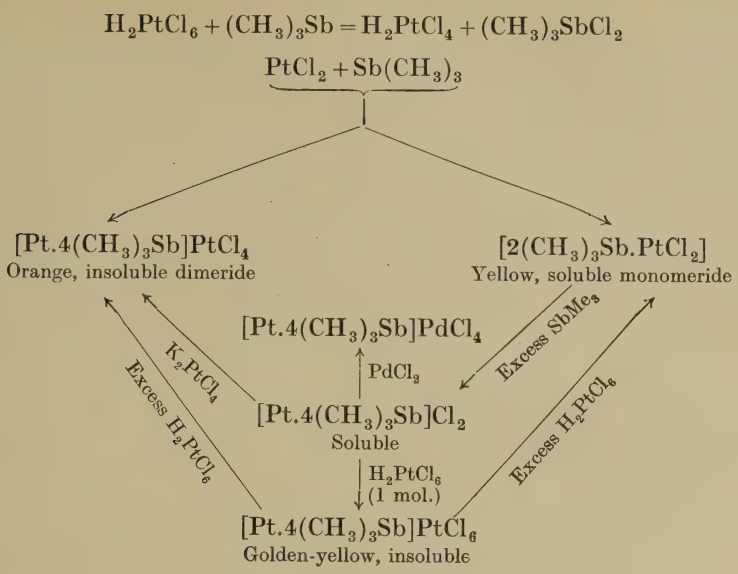
If the foregoing reactions are repeated with tri-*n*-butylstibine, good results are not obtained, only *bistri-n-butylstibinedichloroplatinum* being produced, and analysis shows that the product has undergone extensive decomposition.

In a similar manner the following palladium derivatives are obtained: *Bis-trimethylstibinedichloropalladium*, $[2(CH_3)_3Sb.PdCl_2]$, an orange-yellow deposit at low temperatures, becoming lemon-yellow at ordinary temperature, prolonged warming causing decomposition without melting, metallic palladium separating. During the preparation of this compound the more soluble *tetrakistrimethylstibinepalladous chloride*, $[Pd.4(CH_3)_3Sb]Cl_2$, is produced and separates from the aqueous filtrate as well-defined, golden-orange needles, contaminated with trimethylstibine dichloride. The *tetrakis*-compound is readily soluble in water, but decomposed on boiling. The same compound results when trimethylstibine in excess reacts with *bis*trimethylstibinedichloropalladium. Boiling with dilute hydrochloric acid or a large excess of chloroform converts the *tetrakis*-derivative into a lemon-yellow substance, $[(CH_3)_3Sb.PdCl_3]H$, which, unlike other pallado-compounds, is stable on keeping. It yields a light brown precipitate with cæsium hydroxide.

A summary of the formation of these compounds is given in the scheme on p. 171.

Triethylstibine, $(C_2H_5)_3Sb$, is obtained as follows: (1) By the interaction of an alloy of potassium and antimony with ethyl iodide.[1] (2) By treating antimony trichloride with zinc diethyl.[2] (3) By re-

[1] Löwig and Schweizer, *Annalen*, 1850, 75, 315.
[2] Hofmann, *Annalen*, 1857, 103, 357.



placing the zinc diethyl in (2) by mercury diethyl.[1] (4) By distilling triethylstibine di-iodide with zinc.[2] The stibine is a colourless, strongly refractive liquid, B.pt. 158·5° C. at 730 mm., or about 75° C. at 16 to 18 mm.,[3] density 1·3244 at 16° C.; it does not solidify at −29° C. It has an odour resembling that of onions, and fumes and burn in air with a luminous flame. It is readily soluble in alcohol or ether, but insoluble in water. With fuming hydrochloric acid it is converted into triethylstibine dichloride and hydrogen. It combines slowly with ethyl iodide.

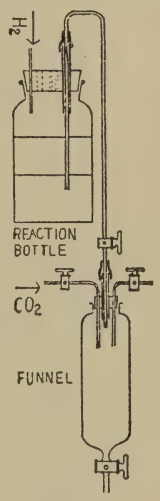


Fig. 2.

Tri-n-propylstibine,[4] $(C_3H_7)_3Sb$, obtained from antimony trichloride and magnesium *n*-propyl bromide, boils at 100° C. at 25 mm., or at 113° C. at 39 mm., density 1·241 at 25° C. The yield from 62 grams of the alkyl bromide is about 11 grams of pure product, which possesses a penetrating, alliaceous odour. The apparatus used for preparing this and the following stibines is as shown in fig. 2. It consists of a wide-necked bottle, of 1 litre capacity, fitted with a rubber stopper carrying a mercury-sealed stirrer, a dropping funnel, a reflux condenser, an inlet tube for hydrogen, and a siphon whereby liquid layers may be withdrawn and separated in the absence of air. The exterior limb of the siphon is fitted with a tap and it slides smoothly through a glass jacket fixed in the stopper of a separating funnel. Air-tightness is secured by stretching rubber tubing over both the jacket and the limb of the siphon. The other limb of the siphon passes into the reaction

[1] Buckton, *Quart. J. Chem. Soc.*, 1863, **16**, 22; *Jahresber.*, 1863, p. 470.
[2] Buckton, *Quart. J. Chem. Soc.*, 1861, **13**, 118; *Jahresber.*, 1860, p. 373.
[3] Grüttner and Wiernik, *Ber.*, 1915, **48**, 1749.
[4] Dyke, Davies and Jones, *J. Chem. Soc.*, 1930, p. 463.

bottle by a similar device, which permits adjustment of the siphon to any desired level. The separating funnel is provided with two tubes with taps to serve either as inlet or outlet, respectively, for carbon dioxide, or for the application of suction.

The Grignard solution is prepared by dropping the freshly prepared alkyl halide, dissolved in 150 c.c. of ether, on to 12·1 grams of magnesium turnings immersed in 150 c.c. of ether to which a granule of iodine has been added. Throughout the preparation of this solution and its interaction with antimony trichloride, pure dry hydrogen is passed over the liquid. The liquid is cooled to 0° C. and 38·1 grams of freshly redistilled antimony trichloride in 100 c.c. of ether are added drop by drop. After the addition is complete the mixture is warmed for half an hour, again cooled to 0° C., and then treated with ammonium chloride solution. The separating funnel is now filled with pure dry carbon dioxide and the ether layer transferred from the reaction bottle to the funnel. In this way an unclouded solution is obtained.

Tri-n-butylstibine, $(C_4H_9)_3Sb$, boils at 131° C. at 12 mm., and has a density of 1·191 at 25° C. *Tri-isobutylstibine*, obtained from magnesium *iso*butyl bromide and antimony trichloride, has B.pt. 135° C. at 31 mm., density 1·323 at 25° C. The first runnings in the distillation of the crude products contain $\beta\epsilon$-dimethylhexane. The butylstibines possess a mixed alliaceous-butyric odour. The *iso*butyl compound is distinctly yellow.

Tri-n-amylstibine, $(C_5H_{11})_3Sb$.—From 76 grams of *n*-amyl bromide about 15 grams of the stibine are produced, B.pt. 168° C. at 16 mm., density 1·136 at 18° C. In this preparation 8 grams of *n*-decane are obtained as a by-product.

Tri-dl-β-methylbutylstibine, $(C_5H_{11})_3Sb$, boils at 150° C. at 14 mm., density 1·242 at 25° C. ; the synthetic action of the magnesium gives $\gamma\zeta$-dimethyloctane in the course of the preparation.

Tri-isoamylstibine or *Tri-γ-methylbutylstibine*, $(C_5H_{11})_3Sb$, may be isolated in two ways : (1) By the interaction of equivalents of antimony trichloride and magnesium *iso*amyl bromide 10 grams of the stibine are obtained, B.pt. 149° C. at 14 mm., density 1·227, and 10 grams of $\beta\eta$-dimethyloctane are formed as by-product. (2) By the interaction of potassium-antimony alloy and *iso*amyl iodide.[1] When distilled in a stream of carbon dioxide under atmospheric pressure, the stibine passes over with considerable decomposition at about 260° C. It fumes in air, but is not spontaneously inflammable. In ether it is readily soluble, sparingly soluble in absolute alcohol, insoluble in water. When heated with *iso*amyl iodide no condensation takes place even at 100° C. All the amylstibines have a predominating amylic smell ; *n*-amylstibine is colourless, but the β- and γ-methylbutylstibines are both yellowish.

Tri-n-hexylstibine, $(C_6H_{13})_3Sb$,[2] boils at 190° C. at 10 mm. with partial decomposition and liberation of antimony. The distillate has a density of about 1·15 at 25° C. The odour resembles that of *n*-hexyl alcohol. *n*-Dodecane is formed as a by-product in the preparation.

[1] Cramer, *Jahresber.*, 1855, p. 590; Berlé, *J. prakt. Chem.*, 1855, 65, 385; *Annalen*, 1856, 97, 316.

[2] Dyke, Davies and Jones, *loc. cit.*

Compounds of the Type R_3SbX_2.

Trimethylstibine oxide, $(CH_3)_3SbO$, occurs when the sulphate, $(CH_3)_3Sb.SO_4$, is treated with barium hydroxide, filtered and evaporated. The residue is taken up in alcohol and the solution evaporated in the absence of carbon dioxide. The oxide forms a white, crystalline mass, very soluble in water or alcohol, insoluble in ether.[1] It is also formed, together with other products, when an ether solution of trimethylstibine is slowly evaporated in air. It forms a *double compound* with the *dichloride*, $(CH_3)_3SbO.(CH_3)_3SbCl_2$,[2] crystallising in regular octahedra, soluble in water or alcohol.

Trimethylstibine dichloride, $(CH_3)_3SbCl_2$, is prepared (1) by treating trimethylstibine in carbon disulphide solution with chlorine,[3] (2) by the interaction of trimethylstibine oxide and hydrochloric acid, (3) by heating trimethylstibine and hydrochloric acid together in a sealed tube, (4) by allowing antimony trichloride and mercury dimethyl to react, when a double compound of trimethylstibine dichloride and methylmercuric chloride is isolated.[4] The dichloride crystallises from water in hexagonal crystals,[5] which dissolve readily in hot alcohol.

Trimethylstibine dibromide, $(CH_3)_3SbBr_2$.—A cold alcoholic solution of the stibine when treated with bromine gives a white crystalline precipitate of the dibromide.[6] The same substance occurs when the di-iodide is treated with mercuric bromide.[7] Sparingly soluble in cold alcohol or water, the dibromide is more soluble when warm solvents are used. It behaves towards sodium hydroxide and phenolphthalein as a free hydrogen halide. Its molecular conductivity $\mu = 500$ to 521 with $v = 64$ to 1024.[8] It forms a *double compound* with the *oxide*, $(CH_3)_3SbO.(CH_3)_3SbBr_2$, which crystallises in needles from alcohol, being sparingly soluble in the cold solvent, readily soluble in water. The molecular conductivity $\mu = 201{\cdot}2$ to $243{\cdot}9$ with $v = 80$ to 1280.

Trimethylstibine hydroxychloride, $(CH_3)_3SbCl.OH$, occurs when trimethylstibine dihydroxide in aqueous solution is treated with concentrated hydrochloric acid. It is soluble in water, separates from ether in minute colourless plates and from alcohol in silky needles.[9] By a similar process a well-defined *hydroxypicrate* is isolated as a pale yellow product.

Trimethylstibine cyanobromide, $(CH_3)_3SbBr.CN$, is formed by the condensation of cyanogen bromide and trimethylstibine in petroleum in an inert atmosphere. An apparatus of special design (p. 169) is used to carry out the preparation. The cyanobromide is a colourless, crystalline solid, insoluble in cold anhydrous organic solvents, but rapidly hydrolysed by moisture to yield the hydroxybromide.

Trimethylstibine hydroxybromide, $(CH_3)_3SbBr.OH$, is a white, crystalline compound, formed as indicated above. It dissolves readily in cold water, and separates from alcoholic solutions as lustrous, white

[1] Landolt, *J. prakt. Chem.*, 1861, 84, [i], 331; *Jahresber.*, 1861, p. 570.
[2] Hantzsch and Hibbert, *Ber.*, 1907, 40, 1508.
[3] Landolt, *loc. cit.*
[4] Buckton, *Quart. J. Chem. Soc.*, 1863, 16, 22; *Jahresber.*, 1863, p. 470.
[5] vom Rath, *J. prakt. Chem.*, 1861, 84, [i], 334.
[6] Landolt, *loc. cit.*
[7] Landolt, *Annalen*, 1852, 84, 44.
[8] Hantzsch and Hibbert, *loc. cit.*
[9] Morgan and Yarsley, *Proc. Roy. Soc.*, 1926, 110, 534.

needles, which decompose without melting. Warming with a suspension of silver oxide for one hour on the water-bath converts the hydroxybromide into *trimethylstibine dihydroxide*, $(CH_3)_3Sb(OH)_2$, consisting of colourless, microscopic crystals, slightly hygroscopic, but otherwise stable.

Trimethylstibine di-iodide, $(CH_3)_3SbI_2$, may be obtained by treating the stibine with iodine in the presence of alcohol [1] or by heating metallic antimony in a sealed tube with methyl iodide at 140° C.[2] It crystallises from water in hexagonal prisms and from alcohol in needles, M.pt. 107° C., being readily soluble in hot water or alcohol, sparingly soluble in ether. Trimethylstibine combines with *cyanogen iodide* in ether solution at −20° C. to give a *compound* which is probably $(CH_3)_3Sb.CNI$; this is, however, readily decomposed, and with water or alcohol is converted into the *double compound* of the *iodide* and *oxide*, $(CH_3)_3SbO.(CH_3)_3SbI_2$,[3] citron-yellow octahedra, decomposing on warming with water.

Trimethylstibine hexaiodide, $(CH_3)_3SbI_6$,[4] occurs when an aqueous solution of the di-iodide is treated with iodine. It forms greenish-black needles, M.pt. 68° to 70° C., and is rather unstable.

Trimethylstibine dicyanide, $(CH_3)_3Sb(CN)_2$, is not a very stable compound, forming as a yellow crystalline precipitate when silver cyanide reacts with the foregoing di-iodide.[5]

Trimethylstibine dithiocyanate, $(CH_3)_3Sb(CNS)_2$, is formed by heating the dichloride in alcohol solution with potassium thiocyanate. It separates as white crystals, readily soluble in hot water and organic solvents, sparingly soluble in cold water.[6]

Trimethylstibine sulphide, $(CH_3)_3SbS$.—An ether solution of trimethylstibine is warmed with sulphur, or an aqueous solution of trimethylstibine oxide is treated with hydrogen sulphide.[7] The sulphide also occurs when an ether solution of trimethylstibine dibromide is treated with potassium ethylate and the filtrate subjected to the action of a current of hydrogen sulphide.[8] It forms crystals from alcohol, M.pt. 168° C. with decomposition, is sparingly soluble in cold water, being more soluble in alcohol or ether.

Trimethylstibine sulphate, $(CH_3)_3SbSO_4$, is the product of interaction of the di-iodide and silver sulphate in hot aqueous solution. It forms a white, semi-crystalline mass, soluble in water, less soluble in alcohol.[9]

Trimethylstibine dinitrate, $(CH_3)_3Sb(NO_3)_2$, may be prepared either by dissolving the stibine in nitric acid or by treating the di-iodide with silver nitrate. It forms colourless crystals, soluble in water or alcohol, insoluble in ether.

In addition to the foregoing salts, the following are mentioned in the literature: *hydrogen sulphate*, quadratic plates; *carbonate*, deliquescent, unstable, yellowish crystals; *bicarbonate*, deliquescent, stellate groups of needles; *acetate*, unstable, dark syrup; *acid tartrate*, very soluble in water; *oxalate*, small deliquescent crystals.[10]

[1] Landolt, *loc. cit.*
[2] Buckton, *Quart. J. Chem. Soc.*, 1861, 13, 119; *Jahresber.*, 1860, p. 374.
[3] Hantzsch and Hibbert, *loc. cit.*
[4] Lowry and Simons, *Ber.*, 1930, 63, [B], 1595.
[5] Landolt, *loc. cit.*
[6] Hantzsch and Hibbert, *loc. cit.*
[7] Landolt, *loc. cit.*
[8] Hantzsch and Hibbert, *loc. cit.*
[9] Landolt, *loc. cit.*
[10] Landolt, *Annalen*, 1852, 84, 44.

Triethylstibine oxide, $(C_2H_5)_3SbO$, is prepared by the following methods: (1) In an impure state by oxidation of triethylstibine either by burning or exposing an ether solution to the air. The by-product is ethylstibinic acid.[1] (2) An aqueous solution of triethylstibine sulphate is treated with barium hydroxide, the barium sulphate removed and the filtrate evaporated on the water-bath. The residue is extracted with alcohol, carbon dioxide passed through the solution, the barium carbonate filtered off and the alcoholic filtrate evaporated. (3) An alcoholic solution of triethylstibine is shaken with finely divided mercuric oxide, free mercury separating out and the organic oxide remaining in solution, from which it may be obtained by evaporation. The oxide separates as a colourless, viscous mass, having a very bitter taste;[2] it may be solidified by drying over concentrated sulphuric acid, but when heated on the water-bath it becomes liquid again. It is readily soluble in water or alcohol, but sparingly soluble in ether. It combines directly with mineral acids, forming salts, and precipitates hydroxides of the metals from salt solutions. An ether solution of the *stibine oxide* reacts with *antimonious oxide* forming an amorphous *compound*, $(C_2H_5)_3SbO.Sb_2O_3$, soluble in water or alcohol, and yielding triethylstibine dichloride on treatment with concentrated hydrochloric acid.[3]

Triethylstibine dichloride, $(C_2H_5)_3SbCl_2$.—Several methods are available for isolating this substance: (1) Chlorine combines directly with triethylstibine, but the reaction is very violent and difficult to control.[4] (2) The stibine may be treated with fuming hydrochloric acid. (3) Concentrated hydrochloric acid is added to a solution of the dinitrate and the whole evaporated down. The dichloride separates as an oil, which is dissolved in alcohol and precipitated by dilution with water. (4) Magnesium ethyl iodide and antimony pentachloride react to form the dichloride.[5] The dichloride is a colourless, highly refractive liquid, density 1·540 at 17° C., and does not solidify at −12° C. It has a bitter taste, a terpenoid odour, is insoluble in water, readily soluble in alcohol or ether, and slightly volatile in steam. Concentrated sulphuric acid decomposes it with evolution of hydrochloric acid. The *double compound* with the *oxide*, $(C_2H_5)_3SbCl_2.(C_2H_5)_3SbO$, is a deliquescent mass, obtained by treating an aqueous solution of the iodide double compound, $(C_2H_5)_3SbI_2.(C_2H_5)_3SbO$, with mercuric chloride.[6]

Triethylstibine dibromide, $(C_2H_5)_3SbBr_2$, occurs when an alcoholic solution of the stibine is treated dropwise with a similar solution of bromine.[7] It is purified by the method described for the dichloride. The dibromide is a colourless, strongly refractive liquid, density 1·953 at 17° C., solidifying to a snow-white mass at −10° C. It has a terpenoid odour, causes violent sneezing and is tear-exciting when warmed. In water it is insoluble, but solutions may be obtained in alcohol or ether. Concentrated sulphuric acid causes evolution of hydrobromic acid, and chlorine displaces bromine.

[1] Löwig and Schweizer, *Annalen*, 1850, 75, 315; Löwig, *ibid.*, 1853, 88, 323.
[2] Compare Merck, *Annalen*, 1856, 97, 329; Strecker, *ibid.*, 1858, 105, 310.
[3] Löwig, *loc. cit.*
[4] Löwig and Schweizer, *loc. cit.*
[5] Pfeiffer and Schnurmann, *Ber.*, 1904, 37, 320.
[6] Merck, *loc. cit.*; Strecker, *loc. cit.*
[7] Löwig and Schweizer, *loc. cit.*

Triethylstibine di-iodide, $(C_2H_5)_3SbI_2$.—An alcoholic solution of triethylstibine is treated with iodine and the solution evaporated to crystallising point. Purification is effected by crystallisation from alcohol or ether. The di-iodide also occurs when ethyl iodide is heated at 140° C. in a sealed tube with coarse metallic antimony.[1] It crystallises in colourless needles, which may be 0·5 in. in length and difficult to purify. It melts at 70·5° C. and sublimes at 100° C., is very soluble in alcohol or ether, less soluble in water. The molten iodide is immediately decomposed by metallic potassium. Chlorine and bromine cause the liberation of iodine, whilst hydrochloric and nitric acids give the dichloride and dinitrate, respectively. The *double compound* with the *oxide*, $(C_2H_5)_3SbI_2.(C_2H_5)_3SbO$, is formed when the di-iodide is treated with alcoholic ammonia [2] or when the di-iodide and oxide are mixed in alcohol ; [3] it crystallises in octahedra or tetrahedra, and mercuric chloride or bromide converts it to the corresponding dichloride or dibromide, respectively.

Triethylstibine sulphide, $(C_2H_5)_3SbS$, may be isolated (1) by treating an ether solution of the stibine with sulphur (a less satisfactory method is to carry out the addition under water) ; [4] (2) by treating an alcoholic solution of the oxide with hydrogen sulphide.[5] It forms a white, silvery mass, M.pt. 100° C., soluble in water, alcohol or warm ether.[6] Above its melting-point it forms volatile products resembling mercaptan, and with metallic potassium some triethylstibine results. With acids hydrogen sulphide is evolved, and from metallic salt solutions the sulphide precipitates sulphides of the metals. Treatment with silver cyanide yields an unstable *dicyanide*.

Triethylstibine selenide, $(C_2H_5)_3SbSe$.—An ether solution of the stibine is boiled with precipitated selenium ; on cooling crystals of the selenide separate. The product soon decomposes in air with precipitation of selenium.

Triethylstibine sulphate, $(C_2H_5)_3SbSO_4$, is best obtained by double decomposition between triethylstibine sulphide and copper sulphate in aqueous solution. Sulphuric acid transforms the oxide and dihalides to the sulphate, but excess of acid hinders crystallisation. The sulphate forms colourless crystals, M.pt. 100° C., very soluble in water, less soluble in alcohol and insoluble in ether. Hydrochloric acid precipitates the dichloride from aqueous solutions of the sulphate. The *double compound* with the *oxide*, $(C_2H_5)_3SbSO_4.(C_2H_5)_3SbO.H_2O$, occurs when the oxyiodide, $(C_2H_5)_3SbI_2.(C_2H_5)_3SbO$, is treated with silver sulphate.[7]

Triethylstibine dinitrate, $(C_2H_5)_3Sb(NO_3)_2$.—When triethylstibine or its oxide is dissolved in dilute nitric acid, the nitrate results. The solution is filtered and evaporated.[8] Nitric acid will also displace the halogen from the dihalides. The dinitrate forms rhombic crystals, M.pt. 62·5° C., solidifying to a crystalline mass at 57° C. It is readily soluble in water or alcohol, sparingly soluble in ether. Its solution has

[1] Buckton, *loc. cit.*
[2] Merck, *loc. cit.*
[3] Strecker, *loc. cit.*
[4] Löwig and Schweizer, *loc. cit.*
[5] Merck, *loc. cit.*; compare Löwig, *loc. cit.*
[6] Löwig and Schweizer, *loc. cit.*
[7] Merck, *loc. cit.*; compare Strecker, *loc. cit.*
[8] Löwig and Schweizer, *loc. cit.*

a bitter taste and is acid to litmus, a characteristic of all the ethyl compounds. It is converted into the dichloride by concentrated hydrochloric acid, but is unaffected by hydrogen sulphide. The *oxynitrate*, $(C_2H_5)_3Sb(NO_3)_2.(C_2H_5)_3SbO.H_2O$, is prepared from the oxyiodide by the action of silver nitrate;[1] it forms a stellate mass, readily soluble in water.

Tri-n-propylstibine oxide, $(C_3H_7)_3SbO$,[2] occurs when an absolute alcohol solution of the stibine is shaken with mercuric oxide. The product is a gelatinous mass, soluble in alcohol and possessing a very bitter taste. When tri-*n*-propylstibine reacts with atmospheric oxygen it yields *tri-n-propylstibinic metantimonite*, $(C_3H_7)_3SbO.Sb_2O_3$, a white solid, unchanged at 220° C.

Tri-n-propylstibine sulphide, $(C_3H_7)_3SbS$.—When dry hydrogen sulphide is passed into an absolute alcohol solution of tri-*n*-propylstibine oxide, a solution results from which the sulphide is deposited as small, yellowish needles, M.pt. 88° C., darkening on exposure to the air. Boiling with acids liberates hydrogen sulphide, stibine also being evolved. The sulphide is decomposed when its alcohol solution is warmed. When a mixture of tri-*n*-propylstibine, powdered rhombic sulphur and water is refluxed for two hours, impure *tri-n-propylstibinic metathioantimonite*, $(C_3H_7)_3Sb(SbS_2)_2$, is isolated. This is a brown solid, insoluble in water, alcohol or ether, blackening at about 180° C., but unmelted at 200° C.

Tri-n-propylstibine dichloride, $(C_3H_7)_3SbCl_2$, is prepared by mixing solutions of chlorine and the stibine in carbon tetrachloride and evaporating off the solvent in a vacuum. It is a mobile liquid with a pleasant odour, decomposed on distillation.

Tri-n-propylstibine dibromide, $(C_3H_7)_3SbBr_2$, occurs when bromine replaces the chlorine in the preceding preparation. The dibromide forms colourless crystals from ether, M.pt. 45° C., but when treated with water it is immediately hydrolysed. Distillation causes deposition of antimony.

Tri-n-propylstibine di-iodide, $(C_3H_7)_3SbI_2$, is obtained in quantitative yield by the foregoing method. It forms a yellow, semi-solid mass.

Tri-n-butylstibine oxide, $(C_4H_9)_3SbO$, prepared in a similar manner to the *n*-propyl compound, is a viscous syrup, possessing a bitter taste and an odour reminiscent of that of linseed. The *tri-n-butylstibinic metantimonite*, $(C_4H_9)_3SbO.Sb_2O_3$, is prepared in the usual way.

Tri-n-butylstibine dichloride, $(C_4H_9)_3SbCl_2$, prepared similarly to the propyl compound, is a spirituous-smelling heavy liquid which decomposes on being distilled.

Tri-n-butylstibine dibromide, $(C_4H_9)_3SbBr_2$.—4 grams of finely powdered antimony and 10 c.c. of *n*-butyl bromide are heated together for thirty hours at 250° C. Extraction of the mass with ether and evaporation away of the solvent gives the bromide as an oil. It may also be prepared by mixing ether solutions of tri-*n*-butylstibine and bromine.

Tri-n-butylstibine di-iodide, $(C_4H_9)_3SbI_2$, isolated from its components in chloroform solution, is a soft, oily solid, slowly decomposed by boiling water.

[1] Merck, *loc. cit.* [2] Dyke and Jones, *J. Chem. Soc.*, 1930, p. 1921.

Tri-n-amylstibine oxide, $(C_5H_{11})_3SbO$, forms a thick syrup, and *tri-n-amylstibinic metantimonite*, $(C_5H_{11})_3Sb(SbO_2)_2$, is an insoluble, infusible white powder.

Tri-n-amylstibine dichloride, $(C_5H_{11})_3SbCl_2$, obtained as an unstable, sweet-smelling liquid, is readily decomposed by water; the corresponding *dibromide* is a white, pasty mass, slowly decomposed by water.

Tri-isoamylstibine oxide, $(C_5H_{11})_3SbO$, is a greenish-yellow mass, formed by the spontaneous evaporation of an ether solution of tri-*iso*amylstibine.[1] It is insoluble in water, sparingly soluble in ether, soluble in absolute alcohol.

Tri-isoamylstibine dichloride, $(C_5H_{11})_3SbCl_2$, occurs when the preceding compound is dissolved in hydrochloric acid. It is a viscous oil, heavier than water, soluble in alcohol or ether, decomposing when heated above 160° C.

Tri-isoamylstibine dibromide, $(C_5H_{11})_3SbBr_2$.—This compound and the corresponding *iodide*, $(C_5H_{11})_3SbI_2$, are obtained by treating the oxide with the respective halogen acids. The iodide is also said to occur when tri-*iso*amylstibine is treated with iodine. Both products resemble the dichloride in properties. The di-iodide yields with silver sulphate an oily product, probably *tri-isoamylstibine sulphate.*

Tri-isoamylstibine dinitrate, $(C_5H_{11})_3Sb(NO_3)_2$, may be isolated by treating either the dichloride or di-iodide with silver nitrate in alcoholic solution. It separates from dilute spirit in white crystals, melting at about 20° C., soluble in aqueous alcohol, insoluble in water or ether.

A *basic tri-isoamyloxide* and corresponding *sulphide* are mentioned in the literature, but their existence seems doubtful.

Quaternary Stibonium Compounds.

Compounds of this class have been known since 1851—that is, three years before the discovery of the first arsonium compound. The initial compounds isolated were the iodides, R_4SbI, owing to the fact that trimethylstibine combines exothermically at room temperatures with methyl iodide to give tetramethylstibonium iodide. In the ethyl series the components require heating to 100° C. before the addition occurs, whilst tetrapropylstibonium iodide cannot be obtained by this method, but is formed when antimony amalgam, Sb_2Hg_3, is heated with propyl iodide at 183° C., the resulting product being a double compound, $(C_3H_7)_4SbI.HgI_2$. Treatment of stibonium iodides with freshly precipitated silver oxide transforms them into hydroxides, from which salts may be formed by the action of acids. The iodides, when evaporated down with hydrochloric acid, yield chlorides, and mercuric salts are capable of producing similar transformations. In addition to stibonium compounds of the type Alk_4SbX, the following types are also known: $Alk'Alk_3SbX$, $ArAlk_3SbX$, $ArAlk'Alk_2SbX$. Those containing aromatic radicals are included here because they are the only stibonium compounds known which contain aromatic groupings. The mixed aliphatic compounds are formed according to the equation

$$Alk_3Sb + Alk'I = Alk'Alk_3SbI$$

[1] Berlé, *J. prakt. Chem.*, 1855, 65, 385; *Annalen*, 1856, 97, 315.

whilst the aliphatic-aromatic derivatives are isolated according to

$$ArAlk_2Sb + AlkI = ArAlk_3SbI$$
$$ArAlk_2Sb + Alk'I = ArAlk'Alk_2SbI$$

The stibonium halides form double compounds with the halides of gold, mercury, bismuth and platinum. Taken on the whole the stibonium compounds are less deliquescent than the arsonium derivatives.

Compounds of the Type Alk_4SbX

Tetramethylstibonium hydroxide, $(CH_3)_4SbOH$.—An aqueous suspension of freshly precipitated silver oxide is shaken with tetramethylstibonium iodide, the mixture filtered and the filtrate evaporated *in vacuo*.[1] A white, deliquescent, crystalline mass results, which is slippery to touch, and has the alkaline characteristics of potassium hydroxide. It is readily soluble in water or alcohol, insoluble in ether; it absorbs carbon dioxide from the atmosphere and precipitates hydroxides of the metals, including barium hydroxide, from aqueous salt solutions. An aqueous solution of the hydroxide fumes with hydrochloric acid and forms neutral and acid crystalline salts with this and other acids. It liberates ammonia from ammonium salts, and after precipitating zinc hydroxide is capable of redissolving it when in excess. It dissolves sulphur, the addition of acid to such a solution liberating hydrogen sulphide. The conductivity of a solution of one gram-molecule of the base in 16 litres of water is 166.[2]

Tetramethylstibonium chloride, $(CH_3)_4SbCl$.—The foregoing hydroxide may be treated with hydrochloric acid or the iodide evaporated down with this acid.[3] The chloride also results when the iodide is treated with mercuric chloride. It forms white, hexagonal plates, very soluble in water or alcohol, sparingly soluble in ether. With *platinic chloride* it forms a *double salt*, $2[(CH_3)_4SbCl].PtCl_4$, orange-yellow crystals, soluble in hydrochloric acid, very sparingly soluble in water, alcohol or ether.

Tetramethylstibonium bromide, $(CH_3)_4SbBr$, formed by the interaction of the iodide and mercuric bromide, separates in colourless crystals, soluble in water or alcohol, but insoluble in ether.

Tetramethylstibonium iodide, $(CH_3)_4SbI$.—Trimethylstibine and methyl iodide combine directly to form the iodide, and the compound may be recrystallised from water. It separates in hexagonal plates, soluble in 3·3 parts of water at 23° C. It dissolves also in alcohol, but only slightly in ether; concentrated hydrochloric or sulphuric acid liberates hydrogen iodide, and chlorine or bromine liberates iodine.

Tetramethylstibonium nitrate, $(CH_3)_4SbNO_3$, occurs when the iodide in aqueous solution is treated with silver nitrate. It separates in small needles, very soluble in water, sparingly soluble in alcohol or ether.[4]

Tetramethylstibonium sulphate, $[(CH_3)_4Sb]_2SO_4.5H_2O$.—This results when the silver nitrate in the preceding preparation is replaced by silver sulphate. Colourless crystals are isolated, M.pt. 150° C., which are soluble in water or alcohol, but insoluble in ether. The requisite amount of sulphuric acid converts the sulphate to an *acid*

[1] Landolt, *Annalen*, 1851, 78, 91; 1852, 84, 44.
[2] Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 301.
[3] Landolt, *loc. cit.* [4] Landolt, *loc. cit.*

sulphate, $(CH_3)_4Sb.HSO_4$, quadratic plates, soluble in water, less soluble in alcohol and sparingly soluble in ether.

Tetramethylstibonium sulphide, $[(CH_3)_4Sb]_2S$.—The hydroxide is converted into the sulphide by the action of hydrogen sulphide. The sulphide is an amorphous green powder, dissolving in water or alcohol, but insoluble in ether. In the air it rapidly undergoes oxidation.

Tetramethylstibonium bicarbonate, $(CH_3)_4Sb.HCO_3$.—When the hydroxide in aqueous solution is saturated with carbon dioxide and the solution evaporated, stellate aggregates of needles separate. The bicarbonate gives no precipitate with neutral magnesium salts.

The following tetramethylstibonium salts are also known: *cyanide*, $C_4H_{12}SbCN.H_2O$, rhombic (*pseudo*-tetragonal) crystals,[1] readily soluble in water or alcohol, insoluble in ether; *ferrocyanide*, $(C_4H_{12}Sb)_4Fe(CN)_6.12H_2O$, monoclinic, prismatic, yellowish crystals, losing their water at 100° C., sparingly soluble in alcohol, insoluble in ether;[2] *ferricyanide*, $(C_4H_{12}Sb)_3Fe(CN)_6.H_2O$, yellowish plates, becoming anhydrous at 100° C.; *chlorate*, $C_4H_{12}SbClO_3$, regular cubes; *iodate*, $C_4H_{12}SbIO_3.2H_2O$, colourless needles; *periodate*, $C_4H_{12}SbIO_4$, regular crystals; *chromate*, $(C_4H_{12}Sb)_2CrO_4$, pale yellow crystals, soluble in water, insoluble in alcohol or ether;[3] *acid chromate*, $C_4H_{12}SbCrO_4H$, red, regular crystals,[4] soluble in hot water, insoluble in alcohol or ether; *platinichloride*, $(C_4H_{12}Sb)_2PtCl_6$, an orange-yellow powder, sparingly soluble in water, insoluble in alcohol;[5] *acetate*, a syrup; *oxalate*, deliquescent crystals, soluble in water or alcohol; *malate*, $(C_4H_{12}Sb)_2C_4H_4O_5$, hexagonal plates, decomposing at 70° C.; *acid tartrate*, needles, sparingly soluble; *antimonyl tartrate*, $(C_4H_{12}Sb)(SbO)C_4H_4O_6$, a white crystalline powder, sparingly soluble in alcohol, insoluble in ether.[6]

Tetraethylstibonium hydroxide, $(C_2H_5)_4SbOH$.—The corresponding iodide is treated with freshly prepared silver oxide in aqueous or alcoholic solution, the silver iodide removed and the liquid evaporated down, the final stages being conducted *in vacuo*.[7] It is a strongly alkaline, viscous liquid, having an intensely bitter taste. It is miscible in all proportions with alcohol and water, insoluble in ether. A very strong base, it turns red litmus blue, liberates ammonia from ammonium salts, precipitates the hydroxides of the heavy metals from salt solutions, and when in excess will redissolve the hydroxides of aluminium and tin. It appears to be somewhat volatile at 100° C. and decomposes on strong heating. With acids it forms neutral salts.

Tetraethylstibonium chloride, $(C_2H_5)_4SbCl$, is most readily prepared by treating the foregoing hydroxide with hydrochloric acid. It separates as deliquescent needles, soluble in water or alcohol. It yields the following *double salts*: with *auric chloride*, $C_8H_{20}SbCl.AuCl_3$, yellow needles, M.pt. 178° C., soluble in alcohol or acetone, insoluble in water or ether;[8] with *mercuric chloride*, $4C_8H_{20}SbCl.3HgCl_2$, a white powder, sparingly soluble in water,[9] $2C_8H_{20}SbCl.3HgCl_2$, white

[1] Fock, *Ch. Kr.*, 25, 348; compare Groth, *Ch. Kr.*, 1, 235.
[2] Groth, *Ch. Kr.*, 1, 330.
[3] Westphal, *Inaug. Dissert. Berlin*, 1895, p. 28.
[4] Groth, *Ch. Kr.*, 2, 310.
[5] Landolt, *loc. cit.*
[6] Westphal, *loc. cit.*
[7] Löwig, *Annalen*, 1856, 97, 322; *J. prakt. Chem.*, 1855, 64, 415.
[8] Partheil and Mannheim, *Arch. Pharm.*, 1900, 238, 174.
[9] Löwig, *loc. cit.*

plates, soluble in water or alcohol, insoluble in ether, $C_8H_{20}SbCl.4HgCl_2$, white crystals from water, M.pt. 141° to 142° C., easily soluble in alcohol or acetone, insoluble in ether;[1] with *bismuth trichloride*, $C_8H_{20}SbCl.BiCl_3$, pale yellow;[2] with *platinic chloride*, $[C_8H_{20}Sb]_2PtCl_6$, yellow crystals, sparingly soluble in alcohol or cold water, readily soluble in hot dilute hydrochloric acid or acetone, insoluble in ether, decomposing at about 141° C.[3]

Tetraethylstibonium bromide, $(C_2H_5)_4SbBr$, prepared in a similar manner to the chloride, forms colourless needles, readily soluble in water or alcohol.[4] It yields a *double salt* with *bismuth tribromide*, $3C_8H_{20}SbBr.2BiBr_3$, a pale yellow product.[5]

Tetraethylstibonium iodide, $(C_2H_5)_4SbI.1{\cdot}5H_2O$.—Triethylstibine and ethyl iodide are heated together in a sealed tube at 100° C. in the presence of water and the resulting solution evaporated on the water-bath.[6] The iodide also occurs as its double salt with mercuric iodide when ethyl iodide is heated with antimony amalgam, Sb_2Hg_3, in a sealed tube at 183° C.[7] It crystallises as large, hexagonal prisms, 100 parts of water dissolving 19·02 parts of anhydrous iodide at 20° C.[8] It is readily soluble in alcohol, sparingly soluble in ether. A second hydrate is known, $C_8H_{20}SbI.\frac{1}{3}H_2O$, which forms white needles, readily soluble in water or alcohol, sparingly soluble in ether.[9] The iodide yields a number of *double salts*: with *mercuric iodide*, $4C_8H_{20}SbI.3HgI_2$, white columns from alcohol, sparingly soluble in the hot solvent, insoluble in water or ether,[10] $2C_8H_{20}SbI.3HgI_2$, melting at about 70° C., and having a similar solubility to the preceding compound; with *bismuth tribromide*, $3C_8H_{20}SbI.2BiBr_3$, a yellow product;[11] $3C_8H_{20}SbI.Bi_2ClI_5$ is also known but no description is given; with *bismuth tri-iodide*, $3C_8H_{20}SbI.2BiI_3$, red, hexagonal plates; with *iodoform*, $C_8H_{20}SbI.CHI_3$, decomposing into its constituents when boiled with water.[12]

Tetraethylstibonium nitrate, $(C_2H_5)_4SbNO_3$, forms long, deliquescent needles.[13] The corresponding *sulphate* yields small, deliquescent crystals. A *hydrosulphide* is obtained by saturating the hydroxide in aqueous solution with hydrogen sulphide; it is a yellow oil, soluble in water or alcohol.

Tetraethylstibonium oxalate, $[(C_2H_5)_4Sb]_2C_2O_4$, is produced by neutralising a solution of the hydroxide with oxalic acid and evaporating down.

The following tetraethylstibonium compounds are also known: *carbonate*, deliquescent crystals; *formate*, hexagonal needles; *acetate*, *succinate*, *tartrate* and *racemate*, all of which are syrups, difficult to crystallise.

Tetrapropylstibonium hydroxide, $(C_3H_7)_4SbOH$.—When the iodide or its double salt with mercuric iodide is treated with freshly prepared silver oxide the base is obtained as a very hygroscopic mass.[14]

[1] Partheil and Mannheim, *loc. cit.*
[2] Jörgensen, *J. prakt. Chem.*, 1871, [ii], 3, 342.
[3] Buckton, *Quart. J. Chem. Soc.*, 1860, 13, 119; compare Partheil and Mannheim, *Jahresber.*, 1860, p. 373.
[4] Löwig, *loc. cit.*
[5] Jörgensen, *loc. cit.*
[6] Löwig, *loc. cit.*
[7] Partheil and Mannheim, *loc. cit.*
[8] Löwig, *loc. cit.*
[9] Partheil and Mannheim, *loc. cit.*
[10] Löwig, *loc. cit.*
[11] Jörgensen, *loc. cit.*
[12] Steinkopf and Schwen, *Ber.*, 1921, 54, [B], 2969.
[13] Löwig, *loc. cit.*
[14] Partheil and Mannheim, *loc. cit.*

Tetrapropylstibonium chloride, $(C_3H_7)_4SbCl$, obtained in the usual manner, separates as hygroscopic needles. It forms the following *double salts*: with *auric chloride*, $C_{12}H_{28}SbCl.AuCl_3$, yellow needles, M.pt. 98° C., readily soluble in acetone or warm alcohol, very sparingly soluble in ether; with *mercuric chloride*, $C_{12}H_{28}SbCl.HgCl_2$, glistening needles from water, M.pt. 120° to 121° C., having a similar solubility to the preceding compound; with *platinic chloride*, $(C_{12}H_{28}Sb)_2PtCl_6$, yellow-red octahedra, decomposing at 133° C., readily soluble in warm water, alcohol or acetone, sparingly soluble in ether. The *picrate* is a yellow, crystalline solid, M.pt. 67·5° C.

Tetrapropylstibonium iodide, $(C_3H_7)_4SbI$, occurs as its double salt with mercuric iodide, $C_{12}H_{28}SbI.HgI_2$, when antimony amalgam, Sb_2Hg_3, is heated with propyl iodide in a sealed tube at 183° C. It may also be obtained by the interaction of propyl iodide and a potassium-antimony alloy. The *mercuri-iodide* mentioned above forms yellow, crystalline columns, M.pt. 103·5° C., readily soluble in acetone, insoluble in water or ether.

Compounds of the Type $Alk'Alk_3SbX$.

Methyltriethylstibonium hydroxide, $(C_2H_5)_3(CH_3)SbOH$, may be obtained by treating the iodide with moist silver oxide, or the sulphate in aqueous solution may be treated with barium hydroxide, the barium sulphate removed and the filtrate evaporated in the absence of carbon dioxide.[1] It is a yellow, non-volatile oil, having a strong alkaline reaction. It dissolves in water or alcohol, liberates ammonia from ammonium salts and precipitates many hydroxides of the metals.

Methyltriethylstibonium chloride, $(C_2H_5)_3(CH_3)SbCl$.—Hot aqueous solutions of the iodide and mercuric chloride when mixed precipitate the *double salt* with *mercuric iodide*, $C_7H_{18}SbI.HgI_2$, and the filtrate from this contains the chloride. The hydroxide or carbonate is converted to the chloride when treated with hydrochloric acid. The chloride crystallises in needles.

Methyltriethylstibonium iodide, $(C_2H_5)_3(CH_3)SbI$.—Triethylstibine is suspended in warm water and treated with methyl iodide until the odour of the stibine disappears. The solution on evaporation to dryness yields colourless, air-stable, hexagonal prisms, soluble in about two parts of water at 20° C., soluble in alcohol, very sparingly soluble in ether. The iodide yields two *double salts* with *mercuric iodide*, $C_7H_{18}SbI.HgI_2$, yellow plates, sparingly soluble in alcohol, insoluble in water, and $2C_7H_{18}SbI.3HgI_2$, crystallising from alcohol in yellow needles, sparingly soluble in ether, insoluble in water.

The following methyltriethylstibonium salts are prepared by the usual methods: *sulphate*, colourless, deliquescent crystals, M.pt. 100° C.; *nitrate*, anhydrous needles, very soluble in water; *carbonate*, syrupy mass; *formate*, needles, sparingly soluble in cold water or alcohol, more soluble in hot water; *acetate*, anhydrous needles, very soluble in water; *butyrate*, similar to the acetate; *normal oxalate*, needles, fairly soluble in water; *acid oxalate*, needles, very soluble in water; *tartrate*, non-crystallisable syrup; and the *hydrosulphide*, an oil.

[1] Friedländer, *Jahresber.*, 1857, p. 423; *J. prakt. Chem.*, 1857, 70, 456.

Methyltri-n-propylstibonium iodide,[1] $(C_3H_7)_3(CH_3)SbI$, occurs when a mixture of 3 c.c. of tri-*n*-propylstibine and 4 c.c. of methyl iodide is kept for a week. Removal of the excess of methyl iodide gives 5·8 grams of the stibonium iodide, M.pt. 140° C., soluble in water or alcohol, insoluble in ether. When the aqueous solution is boiled, stibine is slowly evolved.

Methyltri-n-propylstibonium hydroxide, $(C_3H_7)_3(CH_3)SbOH$, is prepared by dissolving the foregoing methiodide in cold water and shaking the solution with freshly prepared silver oxide. Filtration and removal of the solvent under reduced pressure gives the hydroxide as an oil. The base is soluble in water, absorbs carbon dioxide and reacts alkaline to litmus. It precipitates cupric, stannous, ferric, aluminium and zinc hydroxides from the respective salt solutions.

The stibonium *sulphate* is an oil, readily soluble in water, and the *chloroplatinate*, $[CH_3(C_3H_7)_3Sb]_2PtCl_6$, melting with decomposition at 142° C., is prepared by dissolving the hydroxide in boiling dilute hydrochloric acid, filtering if necessary, and adding an excess of chloroplatinic acid to the hot solution, when, on cooling, the chloroplatinate is deposited as reddish-gold plates.

Ethyltri-n-propylstibonium iodide, $(C_3H_7)_3(C_2H_5)SbI$, when prepared from its components, requires a month for completion of the reaction at the ordinary temperature, but at 100° C. only four hours are required. It yields large white crystals, melting with decomposition at 185° C., and dissolving in water or alcohol. The corresponding *hydroxide* is an oil, which attacks filter-paper; its aqueous solution is alkaline and precipitates the sparingly soluble hydroxides of the metals from salt solutions. The *chloroplatinate*, M.pt. 141° C. (with decomposition), separates from dilute alcohol as stellate clusters of fine, orange-red needles.

Methyltri-n-butylstibonium iodide, $(C_4H_9)_3(CH_3)SbI$, occurs when its components are allowed to stand together for two weeks. It is a viscous oil admixed with crystals. When its alcoholic solution is boiled in air, a precipitate of *tri-n-butylstibinic metantimonite* is slowly produced. The *hydroxide* is an oil and the *chloroplatinate* forms golden plates melting with decomposition at 134° C.

Methyltri-n-amylstibonium iodide, $(C_5H_{11})_3(CH_3)SbI$, requires three months out of contact with air in order to be obtained from its components. It yields a mixture of oil and crystals, soluble in water or alcohol, insoluble in ether. The *hydroxide* absorbs carbon dioxide from the air, reacts alkaline to litmus and is readily soluble in dilute acids. The *sulphate* is an oil, dissolving in water, and the *chloroplatinate* forms glistening brown plates, M.pt. 127° C. (decomposition).

Compounds of the Types $ArAlk_3SbX$ *and* $ArAlk'Alk_2SbX$.

Phenyltrimethylstibonium iodide, $(C_6H_5)(CH_3)_3SbI$.—Phenyldimethylstibine and an excess of methyl iodide react rapidly at room temperatures to yield this iodide and the reaction is completed by boiling under reflux.[2] A quantitative yield of fine snow-white needles is obtained, readily soluble in water or alcohol, sparingly soluble in ether or petroleum ether. When heated to about 235° C. iodine vapour is evolved.

[1] Dyke and Jones, *J. Chem. Soc.*, 1930, p. 1921.
[2] Grüttner and Wiernik, *Ber.*, 1915, **48**, 1759.

The iodide may readily be transformed to the *picrate*,[1] which crystallises from water in needles, M.pt. 153° C., nitration yielding *m-nitrophenyltrimethylstibonium picrate*, $(C_6H_4.NO_2)(CH_3)_3Sb.OC_6H_2(NO_2)_3$, needles, M.pt. 203° C.

Phenyldimethylethylstibonium iodide,[2] $(C_6H_5)(C_2H_5)(CH_3)_2SbI$. —The methyl iodide in the preceding preparation is replaced by an excess of ethyl iodide and the mixture heated in a sealed tube for five hours. The iodide crystallises in white needles, soluble in water or alcohol, insoluble in ether. Towards 150° C. it evolves some iodine vapour, but tends to sublime at 225° C.

Phenylmethyldiethylstibonium iodide, $(C_6H_5)(C_2H_5)_2(CH_3)SbI$, occurs in quantitative yield when phenyldiethylstibine and methyl iodide are heated together in a sealed tube for two hours at 100° C. It crystallises from alcohol as shining white needles, subliming with some previous loss of iodine at 225° C. The solubility is the same as for the preceding compounds. Ethyl iodide does not combine with phenyldiethylstibine even after five hours' heating at 100° C.

Compounds of the Types $RSbX_2$ and R_2SbX.

When compounds of the types R_2SbX_3 and R_3SbX_2 are heated *in vacuo*, alkyl halide is evolved and di- or mono-halogenated stibines produced respectively :

$$R_2SbX_3 = RSbX_2 + RX$$
$$R_3SbX_2 = R_2SbX + RX$$

Water converts methyldichloro- or methyldibromo-stibine to the oxide, and any compound of the type $RSbX_2$ is transformed to the sulphide, RSbS, by the action of hydrogen sulphide. The monohalogenated compounds, R_2SbX, absorb atmospheric oxygen, yielding oxyhalides, R_2SbOX, whilst chlorine and bromine give trihalides, R_2SbX_3, hydrolysis of which yields the corresponding acids, $R_2SbO(OH)_2$.

Methyldichlorostibine, CH_3SbCl_2, occurs when dimethylstibinic chloride, $(CH_3)_2SbCl_3$, is heated in a vacuum of about 600 mm. until no further evolution of methyl chloride takes place.[3] The residual oil on fractionation yields the stibine as an oil, B.pt. 115° to 120° C. at 60 mm., which does not solidify in an ice-chest after standing for several days. It is readily decomposed by water, giving methylstibine oxide.

Methyldibromostibine, CH_3SbBr_2.—Dimethylstibinic bromide loses methyl bromide when allowed to stand in a desiccator and finally yields greyish-white feathery needles of methyldibromostibine. When recrystallised from carbon disulphide and ether the stibine melts at 42° C. It is non-inflammable and non-oxidisable in air, but is hydrolysed in water or alkaline solution.

Methyldi-iodostibine, CH_3SbI_2, arises from the spontaneous decomposition of dimethylstibinic iodide. It crystallises from carbon disulphide in rosettes of bright yellow needles, M.pt. 110° C.

Methylstibinoxide, CH_3SbO.—When the dichlorostibine is agitated with water and the solution kept neutral by occasionally adding alkali,

[1] Ingold, Shaw and Wilson, *J. Chem. Soc.*, 1928, p. 1280.
[2] Grüttner and Wiernik, *loc. cit.*
[3] Morgan and Davies, *Proc. Roy. Soc.*, 1926, 110, 523.

a white amorphous product results, which appears to be the impure oxide. Treatment with hydriodic acid gives the di-iodide.

Methylstibine sulphide, CH_3SbS, is formed by the action of hydrogen sulphide on any of the monomethyl antimonials. It is a lemon-yellow powder, sparingly soluble in carbon disulphide or benzene, and fuses to a resinous mass at about 70° C.

Dimethylchlorostibine, $(CH_3)_2SbCl$, results when trimethylstibine dichloride is heated in a distilling flask at a vacuum of 600 mm. in a current of carbon dioxide. Methyl chloride is evolved and the chlorostibine left as residue is distilled.[1] It is a colourless liquid, B.pt. 155° to 160° C. at 750 mm., having a pungent and very disagreeable odour. Even under a layer of light petroleum it is readily oxidised by slow absorption of dissolved oxygen, and at 40° C. it becomes spontaneously inflammable in air. With chloroplatinic acid it yields an orange precipitate. The oxidation mentioned above leads to the production of *dimethylstibine oxychloride*, $(CH_3)_2SbOCl$, which is a white amorphous substance, having no smell and moderately soluble in hot water, from which it separates unchanged on cooling. Prolonged boiling of the oxychloride for 8 hours causes hydrolysis, amorphous dimethylstibinic acid resulting. If a fairly rapid stream of chlorine be passed for about 10 minutes into 50 c.c. of dry carbon disulphide cooled in ice and salt, about 10 grams of the chlorostibine then added and chlorination continued until the solution begins to develop a brown colour, a white crystalline deposit is obtained. The latter is *dimethylstibinic chloride*, $(CH_3)_2SbCl_3$, which is more stable than the corresponding bromo-derivative, but fairly easily loses methyl chloride, giving a colourless oily liquid.

Dimethylbromostibine, $(CH_3)_2SbBr$.—Trimethylstibine dibromide loses methyl bromide and yields the bromostibine when heated at 80 to 100 mm. pressure in a carbon dioxide atmosphere. Freshly distilled dimethylbromostibine slowly solidifies to a mass of almost colourless crystals, which at first melt indefinitely at 40° C., but when the specimen is kept in air-free vessels, the melting-point rises to 89° C. and the B.pt. is 175° to 180° C. at 750 mm. The compound is extremely oxidisable and special apparatus has been devised for its analysis (p. 261). *Dimethylstibine oxybromide*, $(CH_3)_2SbOBr$, is obtained in a similar manner to the corresponding chloro-compound, which it resembles in properties. Dimethylbromostibine reacts with a solution of bromine in carbon disulphide at −10° C., yielding *dimethylstibinic bromide*, $(CH_3)_2SbBr_3$. This crystallises in feathery needles, which rapidly lose methyl bromide and form methyldibromostibine. Hydrolysis of this bromide, like that of the foregoing oxybromide, leads to the production of white amorphous dimethylstibinic acid.

Dimethyliodostibine, $(CH_3)_2SbI$, occurs when trimethylstibine di-iodide is heated at 60 to 80 mm. pressure. It yields clear yellow flaky crystals, M.pt. 86° C., which are converted by air oxidation to *dimethylstibine oxyiodide*, $(CH_3)_2SbOI$, which is slightly soluble in hot water and slowly hydrolysed in warm solutions.

Dimethylcyanostibine, $(CH_3)_2SbCN$, is prepared in a similar manner to the foregoing compounds, trimethylstibine cyanobromide, $(CH_3)_3SbBrCN$, being heated to about 160° C. in the specially designed apparatus shown.[2] Calculated amounts of cyanogen bromide dissolved

[1] Morgan and Davies, *Proc. Roy. Soc.*, 1926, 110, 523.
[2] Morgan and Yarsley, *loc. cit.*

in petroleum (B.pt. 40° to 60° C.) are introduced through the tap funnel C into the distillation flask D, this vessel being cooled to −5° C. Nitrogen or carbon dioxide is passed through the apparatus to displace air and trimethylstibine is then distilled gradually from the flask A into the receiver B, and thence it is added in appropriate quantity and with constant shaking to the cyanogen bromide in the flask D. The cyanobromide having been prepared, the taps E and F are closed and the light petroleum removed from the flask D by distillation. The distillate is either collected in N or removed from the apparatus by gentle aspiration at the tap M. During this operation care is taken to keep the

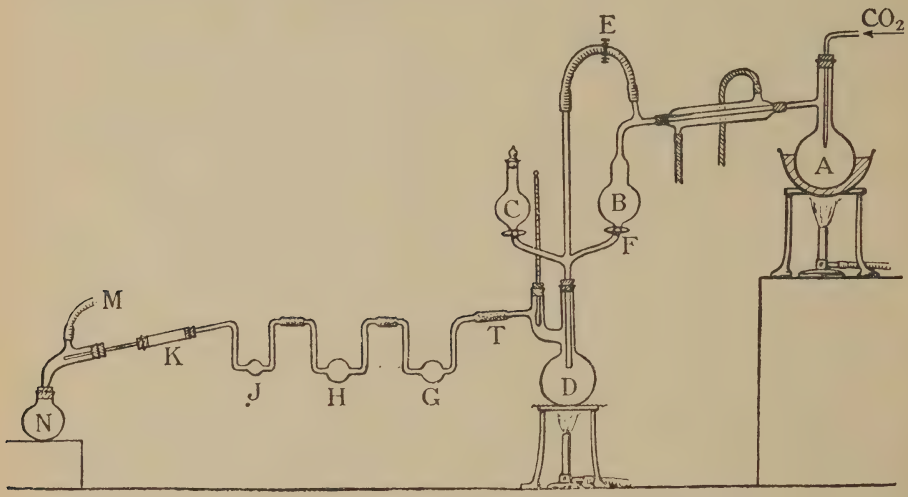


Fig. 3.

condensing bulbs G, H, J and K free from deposited oxide. The apparatus is then exhausted to about 10 mm. pressure, and the flask D, containing the trimethylstibine cyanobromide, is gradually heated to about 160° C., when decomposition of the cyanobromide sets in and a colourless deposit separates in the first bulb G, the intervening tube T, which is packed with glass-wool, being warmed by means of several coils of resistance wire. The bulk of the product which collects in the first bulb G is re-sublimed into the second bulb H, and this operation repeated, so that the solid product of the thermal decomposition is finally collected in a pure condition in the weighed glass cylinder K. By opening the screw clip E nitrogen or carbon dioxide is admitted; the cylinder K is then removed, fitted with rubber stoppers and weighed, air being excluded during this operation. In this way a weighed quantity of the product is isolated in a container readily adaptable to analytical requirements.

The cyanide is a colourless crystalline compound, M.pt. 113° to 114° C., has the nauseating odour of volatile aliphatic antimonials, but beyond exerting a slight irritant action on the eyes and respiratory passages, its effects are not injurious. It is insoluble in water, but readily soluble in alcohol or ether. In air it rapidly oxidises, forming *dimethylstibine oxycyanide*, $(CH_3)_2SbOCN$, a white, crystalline compound,

sintering slightly at 120° C. and decomposing completely at higher temperatures.

Dimethylstibine oxide, $[(CH_3)_2Sb]_2O$, is prepared by treating the corresponding bromide with aqueous sodium hydroxide or saturated aqueous potassium carbonate solution. It is a colourless oil, spontaneously inflammable in the air at ordinary temperatures.[1]

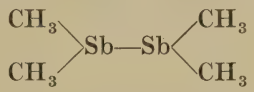
Bisdimethylstibine trisulphide,

$$(CH_3)_2Sb{=}S{-}S{=}Sb(CH_3)_2$$

A suspension of dimethylstibine oxybromide in water is subjected to the action of a rapid stream of hydrogen sulphide. A light yellow precipitate results, this being extracted with carbon disulphide, from which the trisulphide separates as a light yellow powder, M.pt. 76° to 78° C.[2]

Compounds of the Type $R_2Sb.SbR_2$.

Tetramethyldistibine or *Antimony Cacodyl*,[3]



has not been isolated in the pure state, but the following account shows the progress of its investigation to date. Dimethylbromostibine, heated with zinc in sealed tubes filled with carbon dioxide, yields trimethylstibine and some tetramethyldistibine. The latter cannot be separated from the less volatile fractions owing to its decomposition into trimethylstibine and antimony, but it may be identified by adding methyl iodide to the oily mixture. A pale yellow crystalline product separates, and is recrystallised from alcohol, the first crops of crystals consisting of a yellow substance, and the final mother liquors yielding tetramethylstibonium iodide. Repeated crystallisation of the yellow substance from alcohol finally yields bright yellow needles or leaflets having the composition $[2(CH_3)_2SbI.(CH_3)_4SbI.CH_3I]$, confirmed by adding to an excess of methyl iodide one molecular proportion of tetramethylstibonium iodide and two molecular proportions of dimethyliodostibine. Molecular weight determinations of the synthetic product and the original product give values 970 and 1003 respectively.

Tetra-amyldistibine,[4] $[(C_5H_{11})_2Sb]_2$, is said to occur when potassium-antimony alloy, amyl iodide and triamylstibine are allowed to react. This amyl antimony cacodyl is a greenish-yellow aromatic-smelling mobile liquid of bitter taste. It is insoluble in water, miscible in all proportions with alcohol or ether, explodes when heated in oxygen and is decomposed by fuming nitric acid. Evaporation of its ether solution yields an *oxide*, $[(C_5H_{11})_2Sb]_2O$, which has similar properties to the radical itself.

[1] Morgan and Davies, *loc. cit.* [2] Compare Landolt, *Jahresber.*, 1863, p. 571.
[3] Morgan and Davies, *Proc. Roy. Soc.*, 1926, 110, 532.
[4] Berlé, *J. prakt. Chem.*, 1855, 65, 385.

CHAPTER V.

AROMATIC COMPOUNDS OF ANTIMONY.

Compounds of the Type R_3Sb.

Although six types of tertiary aromatic arsines are known, only three varieties of corresponding stibines have been described to date, namely, Ar_3Sb, Ar_2AlkSb and $ArAlk_2Sb$. The most numerous compounds are those of the type Ar_3Sb, and their preparation is effected by the following methods :—

(1) By using the Fittig reaction, antimony trihalides and aryl halides reacting in ether or benzene solution in the presence of sodium in the following manner :

$$3RX + SbX_3 + 6Na = R_3Sb + 6NaX$$

(2) By the interaction of magnesium aryl halides and antimony trihalides :

$$3MgRX + SbX_3 = R_3Sb + 3MgX_2$$

If antimony trisulphide replaces the trihalide the yield is very poor.

(3) In the case of tri-*p*-anisylstibine an aryl halide is allowed to react with sodium antimonide :

$$3RX + Na_3Sb = R_3Sb + 3NaX$$

The yield in this case is poor.

(4) Primary arylstibinoxides are heated in the dry state or in the presence of certain solvents. Antimony trioxide is liberated and secondary arylstibinoxides or tertiary stibines result. Each individual reaction seems to require its own particular set of conditions :

$$3C_6H_5.SbO \xrightarrow[\text{for 4 hours in } CO_2]{\text{Heat at 180° to 200° C.}} (C_6H_5)_3Sb + Sb_2O_3$$

$$3CH_3.CO.NH.C_6H_4.SbO \xrightarrow[\text{in } CO_2]{\text{Reflux in } CH_3OH \text{ for 3 hours}} (CH_3.CO.NH.C_6H_4)_3Sb + Sb_2O_3$$

$$3NH_2.C_6H_4.SbO \xrightarrow[\text{for 1 hour in } CO_2]{\text{Heat at 120° to 125° C.}} (NH_2.C_6H_4)_3Sb + Sb_2O_3$$

Much depends upon the solvent used in this type of reaction. Acetic acid containing tartaric acid converts primary oxides into secondary oxides, so that using these solvents we have the following reaction instead of the first in the three foregoing equations :

$$4C_6H_5.SbO \longrightarrow [(C_6H_5)_2Sb]_2O + Sb_2O_3$$

Several special methods of preparation are worth noting:[1]

(1) A tri-*m*-nitrotriphenylstibinic acid may be reduced by zinc dust and ammonium chloride in alcoholic solution to a tri-*m*-aminotriphenylstibine. The method has also been applied to the preparation of tri-5-aminotri-*m*-xylylstibine.

(2) Tri-5-nitrotri-*m*-xylylstibine dinitrate may be reduced to the stibine by solution in absolute alcohol containing ammonium hydroxide and passing hydrogen sulphide into the boiling solution for six hours. The method may also be used for the *p*-tolyl compound.

(3) Tri-5-nitrotri-*m*-xylylstibine also occurs when tri-6-bromotri-5-nitrotri-*m*-xylylstibine oxide in boiling alcohol is added to a boiling aqueous solution of sodium thiosulphate.

(4) Tri-*m*-iodotri-*p*-tolylstibine and tri-5-iodotri-*m*-xylylstibine are formed by diazotising the corresponding amines and treating the diazonium compounds with potassium iodide.

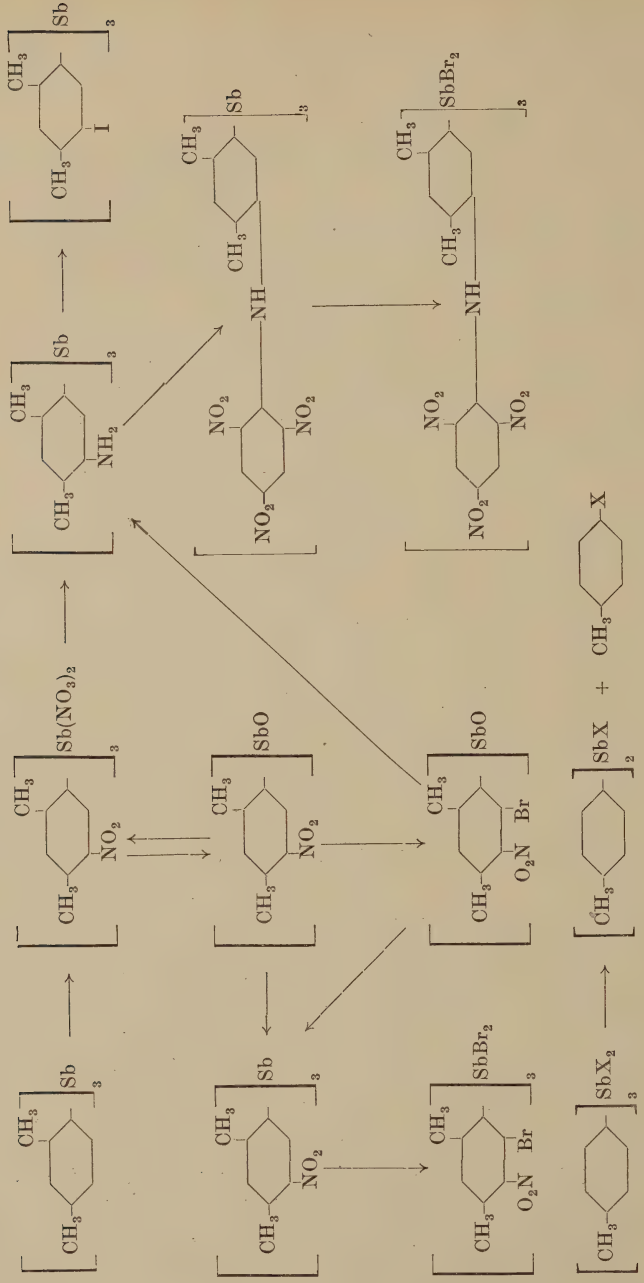
The types $ArAlk_2Sb$ and Ar_2AlkSb are both prepared by the aid of the Grignard reagent:

$$ArSbX_2 + 2AlkMgX = ArAlk_2Sb + 2MgX_2$$
$$Ar_2SbX + AlkMgX = Ar_2AlkSb + MgX_2$$

All the compounds of the type Ar_3Sb are solids, adding on halogens to form dihalides, Ar_3SbX_2. The higher chlorides of copper, iron, thallium, phosphorus and arsenic react with triarylstibines to yield dichlorides, R_3SbCl_2, and the lower chloride of the metal or metalloid. Mercuric chloride combines with the compounds, giving mercurichlorides, and it is noteworthy that whilst tri-*o*-tolylstibine mercurichloride is stable when its alcohol solution is boiled or when the compound is heated at 250° C. in a sealed tube, the corresponding *m*- and *p*-tolyl derivatives and the *p*-anisyl and *p*-phenetyl compounds decompose under these conditions, yielding arylmercuric chlorides, RHgCl. Unlike triphenylarsine, the corresponding stibine does not combine with methyl iodide to give a stibonium compound, but is decomposed, forming trimethylstibine di-iodide, iodobenzene and ethane, whilst zinc dimethyl also disrupts the molecule, giving toluene, antimony and zinc. When triphenylstibine is heated with arsenic, the antimony is replaced by arsenic. Triarylstibines dissolve in concentrated sulphuric acid, yielding sulphates, R_3SbSO_4, and nitration affords trinitro-compounds in which the nitro-groups enter into the ring in the *meta* position to the antimony. Stibines containing amino-groups in the nucleus can be benzoylated, diazotised, and condensed with picryl chloride. In the case of mixed stibines, the type Ar_2AlkSb does not form stibonium compounds, whereas the type $ArAlk_2Sb$ readily combines with alkyl iodides. It should be noted that in this Volume, Part II, p. 72, it was pointed out that tertiary arsines of the type Ar_2AlkAs (where the two aryl groups are identical) show little tendency to form quaternary arsonium compounds. The principal reactions in which tertiary stibines are capable of taking part are illustrated in the following schemes, using *m*-xylyl and *p*-tolyl compounds as examples.[2]

[1] Goddard, *Trans. Chem. Soc.*, 1923, 123, 2319; Goddard and Yarsley, *J. Chem. Soc.*, 1928, p. 719.

[2] Goddard, *Trans. Chem. Soc.*, 1923, 123, 2315; Goddard and Yarsley, *J. Chem. Soc.*, 1928, p. 719.



Compounds of the Type Ar_3Sb.

Triphenylstibine, $(C_6H_5)_3Sb$, may be prepared in a variety of ways: (1) By the Fittig reaction [1]—40 grams of antimony trichloride,

[1] Michaelis and Reese, *Annalen*, 1886, *233*, 45; *Ber.*, 1882, *15*, 2876.

40 grams of chlorobenzene and 50 grams of sodium are allowed to react in 4 volumes of dry benzene. A violent reaction takes place and the mixture may require cooling. Afterwards the whole is boiled for some time on the water-bath and then filtered, the filtrate being concentrated to small bulk. A solid separates, which consists of triphenylstibine with diphenylstibinic chloride and triphenylstibine dichloride as by-products. Treatment with alcoholic hydrochloric acid removes the first of the by-products, and if the residue obtained be then chlorinated in light petroleum, the whole is converted into triphenylstibine dichloride. This product, after crystallisation from alcohol, is dissolved in alcoholic ammonia and reduced by hydrogen sulphide. Triphenylarsine separates out as the solution cools, the heat evolved being due to the reduction process.

A larger scale preparation may be conveniently carried out using the apparatus shown.[1]

A cylindrical steel reaction vessel (3 litres capacity), fitted with a steel cover rendered gas-tight by an asbestos washer, is supported by four upright steel rods fixed in a trough with a waste pipe leading to the sink. Round the outside of the reaction vessel, and near the top, a perforated water-pipe is carried concentrically, and attached to the steel supports. By this means, a stream of cold water can be distributed over the outer surface of the reaction vessel, which may also be heated by a rose burner.

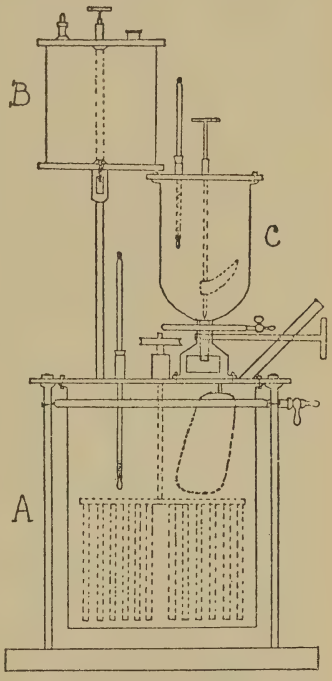


FIG. 4.

The cover of the reaction vessel, A, which is perforated to admit a thermometer, carries also the following fittings :

(*a*) A central steel comb stirrer provided with a pulley for mechanical stirring.

(*b*) A water-cooled steel reflux condenser.

(*c*) A baffle plate projecting into the vessel to assist in the mixing of the contents and to prevent the rotating liquid from splashing up in the condenser.

(*d*) A sodium dropping apparatus, C, consisting of a cylindrical steel container (1 litre capacity) with a curved bottom perforated at its lowest point with an outlet hole (0·6 cm. in diameter). A steel tap and a sight-feed with transparent silica windows attached to the base of the container enable the operator to regulate the flow of molten sodium.

A ring burner placed under the base of the sodium container just above the outlet tap is used to keep the metal in a molten condition. The steel cover of the container, made air-tight with an asbestos washer, carries a thermometer and a hand stirrer, shaped to scour the bottom

[1] Morgan and Vining, *Trans. Chem. Soc.*, 1920, 117, 777.

of the container and provided with a sharp prong to dislodge any obstacle in the outlet tap.

(*e*) A cylindrical glass reservoir, B, for liquid (capacity, 800 c.c.), with steel ends, fitted with a vertical outlet tube to the reaction vessel, a needle valve regulated by a spindle, and a sight-feed with glass window. The steel cover of this reservoir is fitted with a screw-stoppered inlet and with a valve for introducing compressed air, so that the contained liquid is expelled under slight pressure.

Freshly distilled antimony trichloride (344 grams), chlorobenzene (510 grams) and xylene (400 c.c.) are mixed, and the solution is divided equally between the reservoir and the reaction vessel. In the latter case, 600 c.c. of xylene are added as diluent. Sodium (210 grams), covered with 500 c.c. of xylene, is placed in the sodium container, and the preparation of the stibine effected at 70° C. After filtering off in the Bornett press the dark grey, granular sodium chloride, the filtrate, on distilling up to 220° C., leaves a residue of triphenylstibine (M.pt. 48° to 50° C.).

(2) By the Grignard reaction—Antimony chloride (18 grams) as a 10 per cent. solution in benzene is added to the Grignard solution from 50 grams of bromobenzene and 7·2 grams of magnesium in dry ether. The whole is boiled for six hours, then distilled in steam to remove benzene and bromobenzene. The residue is treated with small quantities of alcohol to remove admixed diphenyl, then crystallised from alcohol. The yield is said to be nearly quantitative.[1]

(3) Phenylstibine oxide is heated in an oil-bath at 180° to 200° C. for four hours and a stream of carbon dioxide passed in. The product is extracted with ether, the solvent removed and the solid recrystallised from acetic acid.[2]

Triphenylstibine crystallises as colourless, triclinic plates, M.pt. 48° C.,[3] B.pt. 231° to 232° C. at 16 to 18 mm. or above 360° C. at 760 mm. with partial decomposition. Its density is 1·4998 at 12° C., $\mu_{H\alpha}$ 162·61 at 14° C.[4] It may be purified by conversion into the corresponding sulphide and decomposing the latter (see p. 205). It combines with the halogens, forming dihalides, and it reacts with cupric and ferric chlorides, forming triphenylstibine dichloride and the lower chloride of the metal. It is decomposed by mercuric chloride, forming phenylmercuric chloride and antimony trichloride. With methyl iodide it gives trimethylstibine di-iodide, iodobenzene and ethane; with zinc dimethyl it yields toluene, antimony and zinc. It dissolves in fuming nitric acid, forming tri-*m*-nitrotriphenylstibine dinitrate.[5] When heated with arsenic, triphenylstibine yields triphenylarsine and antimony. It reacts with thallic chloride, yielding thallous chloride and triphenylstibine dichloride.[6] With phosphorus and arsenic trichlorides and with titanium tetrachloride, the main product is triphenylstibine dichloride.[7]

[1] Morgan and Micklethwait, *Trans. Chem. Soc.*, 1911, 99, 2290; see Pfeiffer, *Ber.*, 1904, 37, 4621; Carré, *Bull. Soc. chim.*, 1913, [iv], 13, 102.

[2] Schmidt, *Annalen*, 1920, 421, 242; see German Patent, 389151.

[3] Schmidt, M.pt. 53° C.

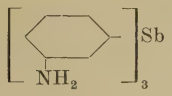
[4] Ghira, *Gazzetta*, 1894, 24, [i], 317.

[5] In addition to dinitrate, some tri-*m*-nitrotriphenylstibine oxide and hydroxynitrate are probably formed.—Author.

[6] Goddard, *Trans. Chem. Soc.*, 1922, 121, 40.

[7] Challenger and Pritchard, *Trans. Chem. Soc.*, 1924, 125, 864.

Tri-m-aminotriphenylstibine,

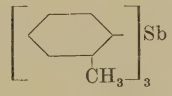


This may be obtained in two ways: (1) Tri-*m*-nitrotriphenylstibinic acid is reduced by zinc dust and ammonium chloride in alcoholic solution, and the mixture filtered into ice-cold water after 30 minutes. The base is collected, converted into the hydrochloride, and re-liberated by ammonium hydroxide.[1] (2) *m*-Aminophenylstibinoxide is heated in a stream of carbon dioxide for about one hour at 120° to 125° C., or until a test portion, oxidised with alkaline hydrogen peroxide and then treated with hydrochloric acid, gives no precipitate of diaminodiphenylstibinic acid. The mass is then extracted with acetone and water added, whereby an oil separates and soon solidifies.

The stibine crystallises from alcohol in bushy needles, M.pt. 124° C.[2] This product is anhydrous, but when recrystallised from glacial acetic acid it melts at about 80° C. and contains 0·5 molecule of water, which may again be removed by recrystallisation from alcohol or heating at 100° C.

Tri-p-acetylaminotriphenylstibine, $(CH_3.CO.NH.C_6H_4)_3Sb$.[3]—*p*-Acetylaminophenylstibinoxide (50 grams) is suspended in 400 c.c. of methyl alcohol and boiled for three hours in a carbon dioxide atmosphere. The liquor is filtered whilst hot and part of the stibine separates on cooling. This is removed, the filtrate evaporated, and the residue extracted with moist acetone, the stibine being precipitated from the extract by the addition of water. The total yield is about 23 grams.[4] The compound exists in three modifications: The *α-form* crystallises from methyl alcohol in needles, sintering towards 205° C., when it becomes turbid, then appears to solidify, and finally melts completely towards 270° C. The *β-form* may be obtained from the *α*-form by recrystallisation of the latter from anhydrous acetone, the resulting product melting at 268° C. When the *α*-form is dissolved in acetone containing a little water, then water added until turbidity is produced, a *γ-form* separates, which sinters at 225° C. This *γ*-form, when crystallised from a large volume of boiling methyl alcohol, is converted into the *α*-form. The three modifications appear to contain the following amounts of water of crystallisation: *α*, 0·5 H_2O; *β*, anhydrous; *γ*, $\frac{2}{3}$ H_2O.

Tri-o-tolylstibine,[5]

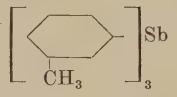


occurs when 51 grams of *o*-bromotoluene, 36 grams of antimony tribromide and 50 grams of sodium are allowed to react in 4 volumes of benzene. When the reaction subsides the mixture is allowed to stand for 4 to 5 days, then filtered, and the residue washed with benzene.

[1] Morgan and Micklethwait, *Trans. Chem. Soc.*, 1911, 99, 2292.
[2] Schmidt, *Annalen*, 1920, 421, 174.
[3] Schmidt, *Annalen*, 1922, 429, 123.
[4] Compare German Patent, 431202.
[5] Michaelis and Genzken, *Annalen*, 1887, 242, 164; *Ber.*, 1884, 17, 924.

The filtrate and washings are concentrated to small bulk and treated with light petroleum, the solid which separates being crystallised from alcohol. It forms fine needles, M.pt. 112° to 113° C., easily soluble in chloroform, benzene or ether, less soluble in alcohol. The *mercurichloride*, $(C_7H_7)_3Sb.HgCl_2$, crystallises in plates, softening at 125° C. and melting at 135° C.; it does not decompose when its alcoholic solution is boiled or when heated at 250° C. in a sealed tube.

Tri-m-tolylstibine,

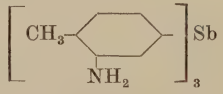


forms colourless crystals from alcohol, M.pt. 67° to 68° C., density 1·3957 at 15·7° C. The yield is 65 per cent. when the preparation is conducted on the same lines as for the foregoing *ortho*-compound. The *mercurichloride* softens at 100° C. and melts with decomposition at 140° C.; when its alcoholic solution is boiled, it yields *m*-tolylmercuric chloride.

Tri-p-tolylstibine,

The same quantities of material are used as for the *ortho*-isomeride, and the mixture worked up after standing for 2 to 3 days. About 25 grams or 63 per cent. of crude product result. The stibine also occurs when antimony tribromide reacts with *p*-tolyl magnesium bromide in ether solution.[1] It forms colourless highly refractive crystals from alcohol, M.pt. 127° to 128° C., density 1·35448 at 15·6° C., readily soluble in chloroform, less soluble in benzene or ether, sparingly soluble in alcohol or light petroleum. The *mercurichloride* is formed when alcoholic solutions of the components are mixed in the cold; if the solutions are boiling, *p*-tolylmercuric chloride results. The mercurichloride crystallises from ether in pearly plates or needles, M.pt. 175° C. with previous sintering at 165° C.

Tri-m-aminotri-p-tolylstibine,[2]



Tri-*m*-nitrotri-*p*-tolylstibine dinitrate (7 grams) is boiled for 8 hours with a solution of 250 c.c. of 90 per cent. alcohol containing 5 grams of ammonium chloride, 15 c.c. of ammonium hydroxide and 15 grams of zinc dust, a further 3 grams of zinc dust being added each hour. The solution is filtered at room temperature into 2 litres of water, the brown solid collected, dissolved in 250 c.c. of warm 15 per cent. hydrochloric acid, and the amine precipitated from the filtered solution by the addition of ammonium hydroxide. When recrystallised from chloroform-light petroleum, a pinkish-grey powder is obtained, M.pt. 92° C.

Tri-m-iodotri-p-tolylstibine, $(C_7H_6I)_3Sb$.—The foregoing amine (3 grams) is dissolved in 20 c.c. of concentrated hydrochloric acid and 200 c.c. of water. The solution is diazotised with 2 grams of sodium

[1] Pfeiffer, *Ber.*, 1904, **37**, 4620.

[2] Goddard and Yarsley, *J. Chem. Soc.*, 1928, p. 719.

nitrite and 5 grams of potassium iodide added. The mixture is then gently warmed for three hours on the water-bath. The precipitate, when crystallised from chloroform-light petroleum, is a reddish-brown powder, sintering at 136° C. and melting at 146° C. to a dark red liquid.

Tri-p-anisylstibine,[1]

This stibine may be obtained in two ways: (1) By the interaction of sodium antimonide and *p*-bromoanisole at high temperatures. (2) By treating antimony trichloride and *p*-bromoanisole with thrice the equivalent quantity of sodium in benzene solution, 200 grams of *p*-bromoanisole giving 68 grams of tri-*p*-anisylstibine. The stibine forms colourless rhombohedra, M.pt. 180·5° to 181° C., easily soluble in chloroform, benzene or toluene, less soluble in alcohol, ether, ethyl acetate, acetic acid or carbon disulphide. When boiled with concentrated hydrochloric acid the stibine decomposes into anisole and antimony trichloride. The *mercurichloride* sinters at 235° to 240° C. and decomposes at 285° C.; prolonged boiling with alcohol converts it into *p*-anisylmercuric chloride.

Tri-p-phenetylstibine,

is prepared in a similar manner to the preceding compound. It forms acicular prisms, M.pt. 82° to 83° C., and is more soluble than the anisyl derivative; it is similarly decomposed by hot concentrated hydrochloric acid. The *mercurichloride* sinters at 205° to 210° C. and decomposes at 225° C.; when boiled with alcohol it yields *p*-phenetylmercuric chloride.

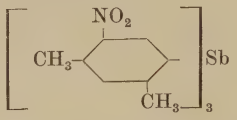
Tri-m-xylylstibine,[2]

This stibine may be prepared in two ways: (1) To the solution prepared from 48 grams of bromoxylene and 7 grams of magnesium in 75 c.c. of ether, 18 grams of antimony trichloride in 25 c.c. of the same solvent are added and the mixture boiled for six hours. The mass is then decomposed with water, the stibine extracted with benzene and worked up as described below. Yield 7·2 grams, or 19 per cent. (2) Bromoxylene (56 grams) and 23 grams of antimony trichloride in 150 c.c. of dry benzene are treated with 50 grams of metallic sodium (thrice the equivalent amount), added in thin slices. The mixture usually requires warming to start the reaction, and after completion is kept overnight, filtered, and the residue extracted three times with boiling benzene, these extracts being added to the main filtrate. Evaporation away of the solvent gives an oily product, which is poured into absolute alcohol, long needles of the stibine separating after a few minutes. The yield of crude product is about 25 grams, or 57 per cent.

[1] Löloff, *Ber.*, 1897, 30, 2834.
[2] Goddard, *Trans. Chem. Soc.*, 1923, 123, 2319.

Tri-*m*-xylylstibine crystallises from alcohol in masses of felted needles, melting at 148° C. to a clear liquid, which becomes cloudy at about 255° C. and, when cooled, solidifies to a transparent mass. It is soluble in cold chloroform, acetone, light petroleum or pyridine, moderately soluble in alcohol, and more soluble than the *para*-compound in glacial acetic acid. The *mercurichloride* crystallises from ether in fine needles, M.pt. 158° C.

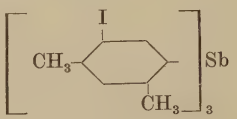
Tri-5-nitrotri-m-xylylstibine,



may be obtained as follows: (1) 2 grams of tri-5-nitrotri-*m*-xylylstibine dinitrate are dissolved in 200 c.c. of absolute alcohol, 20 c.c. of concentrated ammonium hydroxide added, and hydrogen sulphide passed into the boiling solution for six hours. The precipitate is collected and recrystallised from alcohol. (2) Tri-6-bromotri-5-nitrotri-*m*-xylylstibine oxide (1·8 grams) in 40 c.c. of hot absolute alcohol is added to a boiling solution of 1·4 grams of sodium thiosulphate in 25 c.c. of water, and the mixture boiled for 30 minutes. The stibine separates as a white solid. It crystallises from alcohol in small needles, M.pt. 192° to 193° C.

Tri-5-aminotri-m-xylylstibine, $[(CH_3)_2(NH_2)C_6H_2]_3Sb$, is the reduction product of the preceding compound. 5 grams of the mixed nitration products obtained by the action of fuming nitric acid on tri-*m*-xylylstibine are added to a boiling solution of 400 grams of absolute alcohol containing 3·5 grams of ammonium chloride, 20 c.c. of concentrated ammonium hydroxide and 22 grams of zinc dust. The boiling is continued for 8 hours, a further 5 grams of zinc dust being added at the end of each hour. The solution is filtered whilst hot into 3000 c.c. of ice-cold water, a pink precipitate separating out. This is filtered off, dissolved in 200 c.c. of 10 per cent. hydrochloric acid, any insoluble matter filtered off and the filtrate treated with concentrated ammonium hydroxide, when 3·5 grams of crude amine are obtained (97 per cent.). After several crystallisations from chloroform-light petroleum, a brownish-pink powder results, which blackens at about 112° C. and melts rather indefinitely at 123° to 124° C. The *tribenzoyl derivative* melts at 99° C.

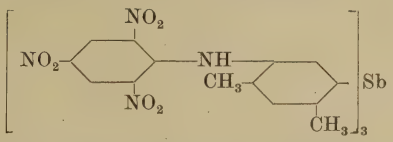
Tri-5-iodotri-m-xylylstibine,



1 gram of the foregoing amine in 7 c.c. of concentrated hydrochloric acid and 200 c.c. of water is diazotised with 0·66 gram of sodium nitrite. The diazonium chloride separates as a yellow precipitate and is treated with 1·5 grams of potassium iodide in 20 c.c. of water. The precipitate changes from yellow to red, and after being warmed on the water-bath and kept for three hours, is filtered off. About 1·5 grams of crude product result, which is crystallised five times from chloroform-

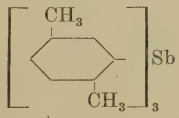
petroleum, a brownish-red crystalline powder resulting. It melts at 153° C. to a clear red liquid.

Tripicryltri-5-aminotri-m-xylylstibine,



2 grams of the amine in the smallest possible quantity of 10 per cent. hydrochloric acid are added to 75 c.c. of alcohol containing 3 grams of picryl chloride and 8 grams of sodium acetate. The mixture is warmed at 30° C. for 15 minutes, an orange precipitate separating (3·9 grams). This is boiled with 75 c.c. of water to remove sodium acetate, then dissolved in dry chloroform to remove sodium picrate, and the stibine is precipitated from the filtered solution by the addition of light petroleum. It forms a bronze, crystalline powder, sintering at 178° C., then blackening but not melting at 290° C. It gives a carmine solution in alcoholic potassium hydroxide, from which the *potassium salt* separates in scarlet octahedral crystals on slow evaporation.

Tri-p-xylylstibine,[1]



To a solution of 24 grams of *p*-bromoxylene and 3·5 grams of magnesium in 50 c.c. of ether, 9 grams of antimony trichloride in 20 c.c. of the same solvent are gradually added. The whole is boiled on the water-bath for four hours, decomposed with water and filtered. The residue is dried and extracted with boiling benzene, evaporation away of the solvent yielding 7·25 grams of short transparent needles, M.pt. 174·5° C., readily soluble in benzene, cold chloroform or boiling glacial acetic acid, moderately soluble in hot acetone, less soluble in ether or alcohol. It reacts with thallic chloride, forming thallous chloride and tri-*p*-xylylstibine dichloride.

Tri-α-naphthylstibine,[2]

To the Grignard reagent from 42 grams of *a*-bromonaphthalene and 5 grams of magnesium in 100 c.c. of ether, 15 grams of antimony trichloride in the same solvent are slowly added with constant agitation. When the reaction subsides it is completed by boiling for one hour on the water-bath, the mixture then being cooled and decomposed by water. The ether is removed, the excess naphthalene distilled off in steam, the residue dissolved in hot benzene and precipitated by adding an equal volume of alcohol. The yield is 15 grams, and after three crystallisations from benzene the product melts at 216° to 217° C. It

[1] Goddard, *Trans. Chem. Soc.*, 1923, **123**, 1170.

[2] Matsumiya, *Mem. Coll. Sci. Kyōtō*, 1925, **8**, 14; see Challenger and Pritchard, *Trans. Chem. Soc.*, 1924, **125**, 868.

is slightly soluble in ether and alcohol, more easily soluble in benzene, carbon disulphide or chloroform. If the antimony trichloride in this preparation be replaced by antimony trisulphide, only a small yield of the stibine is obtained.

Tri-4-biphenylstibine,[1]

To a solution of 100 grams of 4-chlorodiphenyl and 40 grams of freshly distilled antimony trichloride in 500 c.c. of dry benzene, is added an excess (50 grams) of granulated sodium. The mixture requires heating to start the reaction, but after starting it is necessary to cool in ice to moderate the violence of the reaction. When the spontaneous action slackens, the whole is heated for several hours, the product filtered whilst hot, the black residue extracted twice with 250 c.c. quantities of hot benzene and the combined filtrates concentrated to approximately 250 c.c. The addition of an equal volume of warm alcohol causes the entire mass to become semi-solid owing to the separation of crystals. The product is filtered, washed with cold alcohol and dried at 100° C.; yield, 89 grams. It readily dissolves in chloroform, methyl iodide or benzene, separating from the latter as microscopic, hair-like crystals. It melts at 176·5° to 177·5° C. with previous sintering. Decomposition takes place at the boiling-point, with the formation of diphenyl and antimony, among other products.

Compounds of the Types $ArAlk_2Sb$ *and* Ar_2AlkSb.

Phenyldimethylstibine, $C_6H_5.Sb(CH_3)_2$.—Crude phenyldichlorostibine, 25 grams, is added to about 25 grams of magnesium methyl bromide in 250 c.c. of ether. The reaction is completed by boiling the mixture for 30 minutes. The mass is decomposed by water, the ether layer withdrawn and dried over calcium chloride, these and the following operations being conducted in a carbon dioxide atmosphere. The ether is distilled off at the ordinary pressure and the residual oil distilled at 16 to 18 mm. Several fractionations yield a pure product, B.pt. 112° C. at 16 to 18 mm., density 1·4490 at 20° C., n_D 1·5983 at 19·5° C., $n_F - n_C$ 0·02523 at 19·5° C., the yield being 5 to 6 grams.[2] It is a colourless, mobile oil, fuming faintly in air and readily oxidising in solution. It combines with the halogens and alkyl halides in the usual manner.

Phenyldiethylstibine, $C_6H_5.Sb(C_2H_5)_2$, is obtained in a similar manner to the preceding compound, 25 grams of phenyldichlorostibine yielding 6 to 6·5 grams of pure stibine. It is a colourless liquid, B.pt. 128° C. at 16 to 18 mm., density 1·3487 at 24° C., n_D 1·5903 at 21·8° C., and $n_F - n_C$ 0·02373 at 21·8° C. It fumes in air and rapidly oxidises with evolution of heat, its properties resembling those of the methyl derivative.

Diphenylmethylstibine, $CH_3.Sb(C_6H_5)_2$.—25 grams of diphenylchlorostibine in 100 c.c. of anhydrous ether are slowly added to 15 grams of magnesium methyl bromide in 250 c.c. of ether. After boiling the whole for 30 minutes on the water-bath, the mass is decomposed with

[1] Worrall, *J. Amer. Chem. Soc.*, 1930, 52, 2046.
[2] Grüttner and Wiernik, *Ber.*, 1915, 48, 1749, 1759.

water, the ether layer separated in a carbon dioxide atmosphere and dried over calcium chloride. Removal of the solvent and fractionation of the residue in an inert gas yields 10 to 11 grams of pure stibine. It is a colourless, somewhat viscous oil, B.pt. 174° to 177° C. at 16 to 18 mm., density 1·2134 at 20° C., n_D 1·6021 at 20° C., and $n_F - n_C$ 0·02399 at 20° C. It does not fume in air, but readily oxidises. It yields no stibonium compounds with methyl and ethyl iodides even on heating for 10 hours at 100° C., but it combines with chlorine and bromine.

Diphenylethylstibine, $C_2H_5.Sb(C_6H_5)_2$, is obtained in similar yield and by the same process as the preceding derivative. It is a colourless, viscous oil, B.pt. 190° to 192° C. at 16 to 18 mm., density 1·3541 at 19·5° C., n_D 1·6309 at 20·5° C., $n_F - n_C$ 0·02732 at 20·5° C. It has similar properties to the corresponding methyl compound.

Compounds of the Types $R_3SbHal._2$, $R_3Sb(OH)Hal.$, R_3SbO and R_3SbX_2.

The dihalides, $R_3SbHal._2$, may be obtained by heating mercury diphenyl with antimony trichloride at a high temperature in an autoclave, or as by-products in the preparation of triarylstibines by the Fittig reaction. Halogens also add on directly to triarylstibines, giving the dihalides, and in the case of chlorine, the following chlorides may replace the free element in the preparation: copper, iron, thallium, phosphorus or arsenic chloride.

Triphenylstibine dichloride and dibromide undergo hydrolysis with alcoholic alkali, whilst a large bulk of boiling water transforms the dichloride to the hydroxychloride :

$$R_3SbX_2 + H_2O = R_3Sb(OH)X + HX$$

Di-iodides also tend to undergo hydrolysis, forming hydroxyiodides, but the latter are much more readily formed by the action of moisture on the cyanohalides :

$$R_3Sb(CN)X + H_2O = R_3Sb(OH)X + HCN$$

The dihydroxides are obtained from the dihalides by the action of alkali,

$$R_3SbX_2 + 2KOH = R_3Sb(OH)_2 + 2KX$$

or by oxidising the triarylstibines directly by means of alkaline or feebly acid potassium permanganate, or by hydrogen peroxide in the presence of alkali. The products thus obtained are solid, crystalline substances. Alcoholic alkali does not always convert the dihalides to dihydroxides, whilst in some cases the oxide results :

$$R_3SbX_2 \longrightarrow R_3Sb(OH)_2 \longrightarrow R_3SbO$$

The oxides are white, amorphous solids, reacting with acids to form salts.

Dinitrates are formed when the dihalides are treated with alcoholic silver nitrate, or by direct nitration, using fuming nitric acid. In the latter case substitution in the benzene nucleus takes place at the same time and a mixture of products results, the separation of the components usually being impossible. Lead salts have also been used in the same way as silver salts for producing triarylstibine salts.

Unlike triphenylarsine, triphenylstibine does not react directly with sulphur to yield a sulphide, the latter occurring when the dibromide is treated with hydrogen sulphide. Finely divided copper removes the sulphur from a suspension of the sulphide in boiling benzene, yielding pure triphenylstibine. This method is used as a basis for purifying triarylstibines.

Triphenylstibine dichloride, $(C_6H_5)_3SbCl_2$, may be prepared in several ways: (1) By the prolonged heating of antimony trichloride with mercury diphenyl in a sealed tube at 130° C.[1] (2) By treating the stibine in cold petroleum ether with chlorine [2] or with cupric chloride.[3] (3) It occurs as a by-product in the preparation of triphenylstibine by the Fittig reaction.[4] It crystallises in colourless needles, M.pt. 143° C.,[5] soluble in hot alcohol, benzene or carbon disulphide, sparingly soluble in cold alcohol or ether. It is hydrolysed by alcoholic alkali to the *hydroxide*, but is unaffected by water. When an alcoholic solution of the dichloride is added to a large volume of boiling water and the solution evaporated to crystallising point, *triphenylstibine hydroxychloride* separates, $(C_6H_5)_3Sb(OH)Cl$.[6] The hydroxychloride crystallises from benzene in transparent, colourless spicules, M.pt. 218° C.

Triphenylstibine dibromide, $(C_6H_5)_3SbBr_2$,[7] occurs when triphenylstibine in glacial acetic acid is treated dropwise with bromine. It forms needles, M.pt. 216° C., soluble in benzene, carbon disulphide or hot glacial acetic acid, sparingly soluble in other organic solvents.

Triphenylstibine di-iodide, $(C_6H_5)_3SbI_2$, is precipitated when solutions of the stibine and iodine in light petroleum are mixed. It crystallises as pale yellow plates, M.pt. 153° C., soluble in benzene, insoluble in alcohol, ether and light petroleum.

Triphenylstibine in cold, dry, ether solution yields a *cyanoiodide*, $(C_6H_5)_3Sb(CN)I$, when treated with cyanogen iodide.[8] The compound is a pale yellow solid, M.pt. 174° C., and is not very stable, yielding the *hydroxyiodide*, $(C_6H_5)_3Sb(OH)I$, even in dry solvents, hydrogen cyanide being evolved. The hydroxyiodide [9] also occurs when the cyanogen iodide is added to triphenylstibine in ordinary ether. It forms white, satin-like leaflets, M.pt. 196° C., insoluble in ether or light petroleum, but soluble in other organic solvents.

Tri-o-tolylstibine dichloride, $(CH_3.C_6H_4)_3SbCl_2$,[10] is obtained by passing chlorine into a cold ether solution of the stibine. It crystallises from alcohol-chloroform as shining, snow-white needles, M.pt. 178° to 179° C. The corresponding *dibromide* forms colourless crystals, M.pt. 209° to 210° C., and the *di-iodide* pale yellow crystals, M.pt. 174° to 175° C., turning red.

Tri-m-tolylstibine dichloride crystallises from ether as thick needles, M.pt. 137° to 138° C., readily soluble in benzene or chloroform, less soluble in alcohol or acetic acid, sparingly soluble in petroleum

[1] Hasenbaümer, *Ber.*, 1898, **31**, 2911.
[2] Pfeiffer, *Ber.*, 1904, **37**, 4621.
[3] Michaelis and Reese, *Annalen*, 1886, **233**, 39.
[4] Michaelis and Reese, *Ber.*, 1882, **15**, 2876.
[5] $\mu_{H\alpha}$ 183·94 at 20·2° C. (Ghira, *Gazzetta*, 1894, **24**, i, 309, 324).
[6] Morgan, Micklethwait and Whitby, *Trans. Chem. Soc.*, 1910, **97**, 37.
[7] Michaelis and Reese, *Annalen*, 1886, **233**, 49.
[8] Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1513.
[9] Wilkinson and Challenger, *Trans. Chem. Soc.*, 1924, **125**, 860.
[10] Michaelis and Genzken, *Annalen*, 1887, **242**, 164; *Ber.*, 1884, **17**, 924.

ether. The *dibromide* forms colourless crystals from ether, M.pt. 113° C., and the *di-iodide* separates from chloroform-petroleum ether as colourless crystals, M.pt. 138° to 139° C.

Tri-p-tolylstibine dichloride separates from alcohol-benzene as glistening crystals, M.pt. 156° to 157° C., very soluble in chloroform, benzene or ether, less soluble in alcohol and insoluble in petroleum ether. The *dibromide* yields small, glistening crystals, M.pt. 233° to 234° C., and the *di-iodide* is a yellow powder, M.pt. 182° to 183° C. The *di-iodide* undergoes partial hydrolysis on repeatedly boiling in chloroform solution, giving the *hydroxyiodide*, M.pt. 218° to 219° C. If these dihalides are dissolved in alcoholic ammonia and treated with hydrogen sulphide, they are decomposed, with formation of the free stibine :

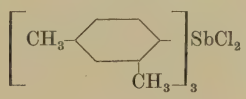
$$(CH_3.C_6H_4)_3SbCl_2 + 4NH_3 + 2H_2S = (CH_3.C_6H_4)_3Sb + 2NH_4Cl + [(NH_4)_2S + S]$$

Tribenzylstibine dichloride, $(C_6H_5.CH_2)_3SbCl_2$, is obtained [1] when magnesium benzyl chloride reacts with antimony trichloride in ether solution.[2] It separates from alcohol as lustrous crystals, M.pt. 105° to 108° C.

Tri-p-anisylstibine dichloride, $(CH_3O.C_6H_4)_3SbCl_2$.[3]—A chloroform solution of the stibine is treated with alcohol and then alcoholic cupric chloride added until no further precipitation of cuprous chloride occurs. The liquid is filtered and the filtrate evaporated, the residue being extracted with benzene, removal of the solvent then yielding the dichloride. The latter is purified by solution in chloroform and re-precipitation with petroleum ether. It forms white crystals, M.pt. 116° to 117° C., which recrystallise from benzene with a molecule of benzene of crystallisation, the melting-point then being 82° to 83° C. The dichloride is readily soluble in benzene, chloroform or ether, sparingly soluble in alcohol and insoluble in petroleum ether. The *dibromide*, obtained from the stibine and bromine in chloroform solution, crystallises in plates, M.pt. 123° C. From benzene the dibromide separates in prisms containing one molecule of solvent and melting at 81° to 82° C. The *di-iodide* forms yellow leaflets, M.pt. 116° C., stable towards water, but appearing to be decomposed by aqueous alcohol.

Tri-p-phenetylstibine dichloride, $(C_2H_5O.C_6H_4)_3SbCl_2$, prepared in a similar manner to the anisyl compound, melts at 84° C., and is sparingly soluble in petroleum ether. The *dibromide* forms fine needles, M.pt. 110° to 111° C., and the *di-iodide*, prismatic crystals, M.pt. 121° to 122° C., both compounds having similar solubilities to tri-*p*-anisylstibine dichloride.

Tri-m-xylylstibine dichloride,[4]

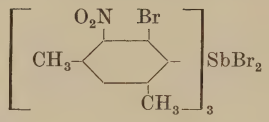


A chloroform solution of the stibine is saturated in the cold with dry chlorine and allowed to evaporate spontaneously. The dichloride

[1] Morgan and Micklethwait, *Proc. Chem. Soc.*, 1912, **28**, 69.
[2] It is asserted (German Patent, 466364) that this reaction yields antimony tribenzyl.
[3] Löloff, *Ber.*, 1897, **30**, 2834.
[4] Goddard, *Trans. Chem. Soc.*, 1923, **123**, 2319.

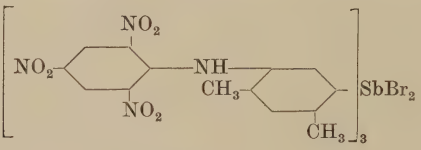
forms small, white, granular crystals, M.pt. 189° C. The *dibromide* is a crystalline powder, M.pt. 195° C.

Tri-6-bromotri-5-nitrotri-m-xylylstibine dibromide,



This is obtained in the usual manner and separates from chloroform-light petroleum as a white crystalline powder.

Tripicryltri-5-aminotri-m-xylylstibine dibromide,



separates from chloroform-light petroleum as a lemon-yellow, crystalline powder. It blackens at 183° C. and melts at 188° C. It dissolves in alcoholic potassium hydroxide, giving a carmine solution, from which the *potassium salt* separates as scarlet crystals.

Tri-p-xylylstibine dichloride, $(C_8H_9)_3SbCl_2$.[1]—To a solution of 2·17 grams of the stibine in 30 c.c. of benzene, 1·55 grams of thallic chloride are added and the solution kept overnight. The thallous chloride is then filtered off, the filtrate evaporated to small bulk and treated with light petroleum, when the dichloride, 1·3 grams, separates. It is a crystalline powder, soluble in cold chloroform, acetone or benzene, moderately soluble in pyridine and insoluble in light petroleum.

Tri-α-naphthylstibine dichloride, $(C_{10}H_7)_3SbCl_2$,[2] is prepared by treating the stibine in ether-benzene or carbon tetrachloride with chlorine. It forms colourless crystals from ether-benzene, M.pt. 256° C., slightly soluble in benzene or chloroform, sparingly soluble in carbon disulphide, practically insoluble in ether, alcohol and petroleum ether. The *dibromide* is prepared in carbon disulphide solution and separates as pale yellow crystals, M.pt. 232° C.[3]

Tri-biphenylstibine dichloride, $(C_6H_5.C_6H_4)_3SbCl_2$.[4]—Tri-biphenylstibine dihalides are obtained by dissolving 5 grams of the stibine in 20 c.c. of pure dry chloroform, adding slightly less than the theoretical amount of the corresponding halogen in chloroform and filtering off the resulting precipitate. Other methods do not yield a white product. The compounds contain chloroform of crystallisation and melt with preliminary softening and decomposition. The dichloride forms small prisms, M.pt. 273° to 274° C.; the *dibromide* gives narrow plates, M.pt. 259° to 260° C.; the *di-iodide* yields small plates, M.pt. 176° to 178° C.

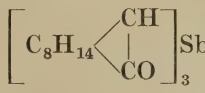
[1] Goddard, *Trans. Chem. Soc.*, 1923, **123**, 1170.

[2] Matsumiya, *Mem. Coll. Sci. Kyōtō*, 1925, 8, 11; Challenger and Pritchard, *Trans. Chem. Soc.*, 1924, **125**, 868.

[3] Challenger and Pritchard (*loc. cit.*) give the melting-points as follows: *dichloride*, M.pt. 260° C., *dibromide*, M.pt. 229° C. with decomposition.

[4] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2046.

Tricamphorylstibine dichloride,[1]



When a toluene solution of antimony trichloride is added to a solution of sodium camphor in the same solvent, heat is generated and a bulky precipitate separates. The mixture is warmed on the water-bath, allowed to stand for a few days, and then treated with water, when antimony oxide separates and is filtered off. The filtrate is steam distilled, the residue extracted with benzene and the solution concentrated. Ice-like crystals separate and light petroleum is added to aid precipitation. Recrystallisation from benzene yields the pure stibine dichloride. The melting-point is 244° C., although on rapid heating the product may remain unchanged at 247° to 248° C. The dichloride gives the value 367·3° for the rotation $[\alpha]_D$ at 20° C. in chloroform solution. It is sparingly soluble in alcohol, insoluble in water, and may be boiled with 2*N* hydrochloric acid without decomposition. On warming with 2*N* sodium hydroxide, the chloride is readily hydrolysed into antimonic and hydrochloric acids and camphor. When heated with aqueous sodium bicarbonate at 55° C. the chloride is destructively hydrolysed, and a similar result is obtained with ammonium hydroxide or alcoholic silver nitrate.

Triphenylstibine dihydroxide, $(C_6H_5)_3Sb(OH)_2$, may be isolated in several ways: (1) Triphenylstibine dibromide is added to warm alcoholic potassium hydroxide and the mixture boiled to complete the reaction.[2] (2) Triphenylstibine is boiled for three hours with alkaline permanganate solution or warmed on the water-bath with an excess of 1 per cent. permanganate solution and dilute sulphuric acid, the permanganate being added from time to time. The solution is finally evaporated and the residue extracted with alcohol, which dissolves the dihydroxide.[3] (3) It may be obtained in crystalline form by adding an alcoholic solution of triphenylstibine dichloride to an equal volume of 2*N* sodium hydroxide solution and allowing the mixture to stand for a few days, when it separates out. (4) Triphenylstibine, in solution or in suspension, is treated with 3 per cent. hydrogen peroxide in the presence of dilute potassium hydroxide, or with sodium peroxide.[4]

The dihydroxide crystallises in leaflets, M.pt. 212° C., soluble in alcohol or glacial acetic acid, insoluble in ether or petroleum ether.

Triphenylstibine diacetate, $(C_6H_5)_3Sb(OCOCH_3)_2$.[5]—Triphenylstibine in acetone solution is oxidised by 3 per cent. hydrogen peroxide and the oxidation product filtered off, dried and recrystallised from glacial acetic acid. The diacetate melts at 215° C., is readily soluble in warm methyl alcohol, and is converted to the corresponding dichloride by hydrochloric acid.

Triphenylstibine dibenzoate, $(C_6H_5)_3Sb(OCOC_6H_5)_2$,[6] is prepared by the interaction of the stibine and benzoyl peroxide in light petroleum

[1] Morgan, Micklethwait and Whitby, *Trans. Chem. Soc.*, 1910, 97, 36.
[2] Michaelis and Reese, *Annalen*, 1886, 233, 49.
[3] May, *Trans. Chem. Soc.*, 1910, 97, 1956.
[4] German Patent, 360973.
[5] Schmidt, *Annalen*, 1922, 429, 123.
[6] Challenger and Wilson, *J. Chem. Soc.*, 1927, p. 209.

solution, or from the dichloride and silver benzoate. It is a solid, M.pt. 171·5° C.

Triphenylstibine dinitrate, $(C_6H_5)_3Sb(NO_3)_2$,[1] obtained by the action of nitric acid on the dihydroxide, crystallises in plates, M.pt. 156° C., soluble in hot concentrated nitric acid or alcohol, insoluble in water.

When triphenylstibine dichloride is treated with alcoholic silver nitrate, a *hydroxynitrate*, $(C_6H_5)_3Sb(OH)NO_3$, results.[2] This crystallises from boiling water in colourless leaflets, softening at 220° C. and melting at 224° to 225° C. It is reduced by Devarda's alloy in the presence of ammonium hydroxide to triphenylstibine and ammonia.

Triphenylstibine sulphate, $(C_6H_5)_3SbSO_4$.[3]—Triphenylstibine and concentrated sulphuric acid are heated together on the water-bath until reaction is complete, the product then filtered off on asbestos, washed with cold alcohol, and afterwards extracted with this solvent. Small crystals are obtained, which are unmelted at 300° C. and are soluble in concentrated sulphuric acid and most organic solvents. The sulphate is decomposed by warm aqueous sodium hydroxide, giving triphenylstibine dihydroxide.

If triphenylstibine dichloride is treated with alcoholic silver sulphate, the *hydroxysulphate* is obtained, $[(C_6H_5)_3Sb(OH)]_2SO_4$.[4] This forms colourless, nodular crystals, M.pt. 252° C. with decomposition, insoluble in cold water, soluble in cold concentrated sulphuric acid. Sulphonation of the hydroxysulphate, using equal volumes of concentrated sulphuric acid and 20 per cent. "oleum" at 100° C. for three hours, then adding an equal volume of "oleum" and allowing to stand for twelve hours, yields *triphenylstibine dihydroxide trisulphonic acid*, $(HO)_2Sb(C_6H_4.SO_3H)_3.3H_2O$. This acid is isolated through its *barium salt*, the free acid being a brittle yellow mass resembling amber. Trituration with phosphorus pentachloride, and then water, gives a *hydroxychloride*, $(C_6H_4.SO_2Cl)_3SbCl(OH)$, decomposing indefinitely at 110° C.[5]

Triphenylstibine dithiocyanate, $(C_6H_5)_3Sb(CNS)_2$.[6]—Triphenylstibine (5 grams) is dissolved in 72 c.c. of a solution obtained from 7·5 grams of lead thiocyanate, 3 grams of bromine and 100 c.c. of dry ether. Light petroleum is added after five hours, the dithiocyanate separating. It forms broad white needles from alcohol, M.pt. 105° to 106° C., soluble in the usual organic solvents, except light petroleum. At 250° C. it decomposes, giving an odour of phenyl thiocyanate.

Triphenylstibine dichloride reacts with lead thiocyanate in dry benzene on prolonged shaking, yielding a *hydroxythiocyanate*, $(C_6H_5)_3Sb(OH)CNS$, a white solid, M.pt. 221° to 225° C. This has a similar solubility to the dithiocyanate, into which it is converted when treated with an excess of thiocyanic acid in ether.

Triphenylstibine dicyanate,[7] $(C_6H_5)_3Sb(CNO)_2$, is obtained from the dichloride and silver cyanate. It is a white crystalline product, M.pt. 111° to 112° C.

Triphenylstibine sulphide, $(C_6H_5)_3SbS$.[8]—A stream of hydrogen

[1] Michaelis and Reese, *loc. cit.*
[2] Morgan, Micklethwait and Whitby, *Trans. Chem. Soc.*, 1910, 97, 36.
[3] May, *loc. cit.*
[4] Morgan, Micklethwait and Whitby, *loc. cit.*
[5] Morgan and Micklethwait, *Trans. Chem. Soc.*, 1911, 99, 2286.
[6] Challenger, Smith and Paton, *Trans. Chem. Soc.*, 1922, 123, 1046.
[7] Challenger and Wilson, *loc. cit.*
[8] Kaufmann, *Ber.*, 1908, 41, 2762; German Patents, 223694, 240316; American Patent, 1060765; Magidson and Süsskind, *Trans. Sci. Chem.-Pharm. Inst. Moscow*, 1923, 6, 21.

sulphide is passed into a filtered solution containing 10 grams of triphenylstibine dibromide in about 160 c.c. of saturated alcoholic ammonia. The liquor is well stirred during the operation and the gas stream is discontinued when a faint yellow coloration is produced, which disappears on shaking. The precipitated sulphide is collected, washed with a little alcohol and then petroleum ether, and dried in air, the yield being about 80 per cent. If the dibromide be replaced by the dichloride, the operation must be carried out in boiling solution. The sulphide forms colourless crystals, M.pt. 119° to 120° C., readily soluble in benzene, chloroform or acetic acid, sparingly soluble in alcohol (1 part in 120 parts of absolute alcohol at the ordinary temperature and in 100 parts at the boiling-point), very sparingly soluble in ether or petroleum ether. Prolonged heating or dilute acids convert the sulphide into triphenylstibine and sulphur. It may also be transformed into triphenylstibine in the following manner, which is a useful way of purifying the stibine : 100 grams of the sulphide in a mixture of 450 c.c. of absolute alcohol and 50 c.c. of benzene are heated under reflux for 30 minutes, then treated with 35 grams of finely divided copper (" Naturkupfer C ") and the boiling continued for three hours. The hot solution is filtered and evaporated, when pure triphenylstibine results. The process gives an 80 to 90 per cent. yield. The copper may be replaced by iron powder.

The preparation of the sulphide from the dihalides by hydrogen sulphide in ammoniacal alcoholic solution requires some care or the reaction goes beyond the stage required and decomposition products result. The dihydroxide probably is first formed, $(C_6H_5)_3Sb(OH)_2$, and this reacts with the hydrogen sulphide as follows :—

$$(C_6H_5)_3Sb(OH)_2 + H_2S = (C_6H_5)_3SbS + 2H_2O$$

Decomposition may take place owing to the following reaction occurring :

$$(C_6H_5)_3SbS + NH_4SH = (C_6H_5)_3Sb\begin{matrix}SNH_4\\SH\end{matrix}$$

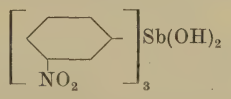
It has also been suggested that a sulphur derivative of the constitution

$$(C_6H_5)_3Sb = S = S\begin{matrix}NH_4\\H\end{matrix}$$

may be formed.

Triphenylstibine hydroxyselenocyanide, $(C_6H_5)_3Sb(OH)(SeCN)$,[1] is the product of the interaction of triphenylstibine dichloride and potassium selenocyanate or cyanogen triselenide. It forms colourless needles, M.pt. 178° C. When heated it yields phenyl selenocyanide, and with hydrochloric acid gives triphenylstibine dichloride.

Tri-m-nitrotriphenylstibine dihydroxide,



This dihydroxide may be prepared in two ways : (1) Triphenylstibine is slowly added to a mixture consisting of 1 part of nitric acid and

[1] Challenger, Peters and Halévy, *J. Chem. Soc.*, 1926, p. 1648.

3 parts of sulphuric acid maintained at 40° C., and the resulting solution diluted with water, the temperature being kept below 25° C.[1] (2) Triphenylstibine hydroxynitrate is nitrated with "mixed acid," first at 40° C. and subsequently at 55° C.[2] The dihydroxide crystallises as pale yellow leaflets, M.pt. 190° to 191° C., soluble in glacial acetic acid, less soluble in alcohol or ether, insoluble in benzene, light petroleum and water. It does not yield ammonia when treated with Devarda's alloy. Under the action of alcoholic hydrochloric acid it gives a mixture of dichloride and hydroxychloride. Its alcoholic solution, when reduced by zinc dust and ammonium chloride, yields tri-*m*-aminotriphenylstibine. The dihydroxide forms alkali salts, which dissolve to brownish-orange solutions in water, acquiring an odour of nitrobenzene on boiling. Other salts of the metals are only sparingly soluble. The dry *sodium salt*, when heated with phosphorus pentabromide, bromine and triethylamine in chloroform solution at 130° to 160° C., yields 1-bromo-3-nitrobenzene in 70 per cent. yield.

Tri-p-acetylaminotriphenylstibine hydroxide, $(CH_3.CO.NH.C_6H_4)_3SbO.4H_2O$.[3]—The α-modification of tri-*p*-acetylaminotriphenylstibine (8·5 grams) is dissolved by boiling with 600 c.c. of methyl alcohol. The solution is rapidly cooled and 30 c.c. of 3 per cent. hydrogen peroxide added. The product is isolated by adding hydrochloric acid and a large bulk of water, when the chloride, sintering at 170° C., is precipitated. This is filtered off and suspended whilst still moist in a little methyl alcohol, cooled in ice, and a small excess of sodium hydroxide added until solution occurs. The whole is then poured into water, when the hydroxide is precipitated. It is a colourless substance, melting at 200° C. when precipitated from aqueous methyl alcohol, but from the hot dry solvent it crystallises in a modification which darkens towards 250° C. The variety of melting-point 200° C. is insoluble in alkali ; both modifications yield the chloride on treatment with alcoholic hydrogen chloride.

Tri-o-tolylstibine oxide, $(CH_3.C_6H_4)_3SbO$,[4] occurs when the dibromide is treated with alcoholic caustic alkali. It is a white amorphous powder, melting at about 220° C., and is converted to the dichloride by hydrochloric acid.

Tri-m-tolylstibine oxide is prepared in a similar manner to the foregoing compound. It is a yellowish-white amorphous powder, softening at 185° C. and melting at about 210° C., insoluble in water, slightly soluble in alcohol, benzene, chloroform or ether. When dissolved in glacial acetic acid it is converted into a *basic acetate*, $(CH_3.C_6H_4)_3Sb(OH)O.CO.CH_3$, M.pt. 142° to 143° C., soluble in benzene, sparingly soluble in the usual organic solvents, insoluble in petroleum ether. An attempted preparation of tri-*m*-tolylstibine by the Grignard reaction gave only *tri-m-tolylstibine hydroxychloride*, a white powder, M.pt. 209° C.[5]

Tri-m-tolylstibine sulphide, $(CH_3.C_6H_4)_3SbS$,[6] occurs when an alcoholic ammoniacal solution of the dichloride is treated with hydrogen sulphide. It crystallises from alcohol in needles, M.pt. 162° to 163° C.,

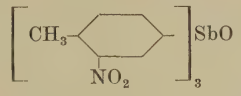
[1] May, *Trans. Chem. Soc.*, 1910, 97, 1956.
[2] Morgan and Micklethwait, *loc. cit.*
[3] Schmidt, *Annalen*, 1922, 429, 135.
[4] Michaelis and Genzken, *Annalen*, 1887, 242, 164.
[5] Challenger and Pritchard, *Trans. Chem. Soc.*, 1924, 125, 864.
[6] Michaelis and Genzken, *loc. cit.*

sparingly soluble in organic solvents with the exception of benzene and chloroform. In the latter solvent the sulphide is transformed to dihalide when treated with halogens.

Tri-p-tolylstibine dihydroxide, $(CH_3.C_6H_4)_3Sb(OH)_2$,[1] is formed by treating a solution or suspension of tri-*p*-tolylstibine with 3 per cent. hydrogen peroxide in the presence of dilute potassium hydroxide, or with sodium peroxide. It is a crystalline product, M.pt. 225° C.

Tri-p-tolylstibine oxide [2] is a white amorphous powder, melting at about 220° C., readily soluble in alcohol, benzene or chloroform, sparingly soluble in ether or petroleum ether. Glacial acetic acid converts it into the *basic acetate*, M.pt. 168° to 169° C.,[3] and a *formate* has also been isolated but not analysed.

Tri-m-nitrotri-p-tolylstibine oxide,[4]



The dinitrate is heated for 8 hours with phosphorous acid in absolute alcohol and the mixture then poured into water. The oxide is recrystallised from alcohol; it is a white powder, softening at 220° C. and melting at 225° C.; at higher temperatures it becomes black.

Tri-m-nitrotri-p-tolylstibine dinitrate, $(C_7H_6.NO_2)_3Sb(NO_3)_2$. —Tri-*p*-tolylstibine is slowly added to the calculated quantity of well-cooled fuming nitric acid and the solution poured into water. The dinitrate is a light, cream-coloured powder, melting at 182° C. after several recrystallisations from alcohol. When heated with bromine and phosphorus pentabromide in chloroform solution for four hours at 130° C., it yields 4-bromo-2-nitrotoluene.

Tri-p-anisylstibine oxide, $(CH_3O.C_6H_4)_3SbO$,[5] formed by decomposing the dihalides with alkali, yields crystalline crusts from alcohol, M.pt. 191° C., very soluble in benzene, ether or chloroform, less soluble in alcohol. Halogen acids convert it to dihalide.

Tri-p-anisylstibine dinitrate, $(CH_3O.C_6H_4)_3Sb(NO_3)_2$, occurs when the dibromide is treated with alcoholic silver nitrate. It forms small needles, M.pt. 217° C. with decomposition.

Tri-p-phenetylstibine dinitrate, $(C_2H_5O.C_6H_4)_3Sb(NO_3)_2$, melts at 151° to 152° C. and decomposes at 170° C.

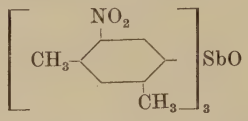
Tribenzylstibine oxide, $(C_6H_5.CH_2)_3SbO$, is obtained by hydrolysing the dichloride with weak alkali. It decomposes indefinitely at 240° C.[6]

Tribenzylstibine dihydroxide, $(C_7H_7)_3Sb(OH)_2$.[7]—The product obtained by the interaction of antimony trichloride (1 mol.), benzyl chloride (3·3 mols.) and magnesium (3·5 atoms) in dry ether is extracted with 12 per cent. aqueous sodium hydroxide and the insoluble residue shaken with ether or distilled with steam. The residue is dissolved in boiling alcohol and the solution treated with water, the precipitated

[1] German Patent, 360973.
[2] Michaelis and Genzken, *loc. cit.*
[3] German Patent, 360973, gives M.pt. 165° C.
[4] Goddard and Yarsley, *J. Chem. Soc.*, 1928, p. 719.
[5] Löloff, *Ber.*, 1897, 30, 2840.
[6] Morgan and Micklethwait, *Proc. Chem. Soc.*, 1912, 28, 69.
[7] Challenger and Peters, *J. Chem. Soc.*, 1929, p. 2610.

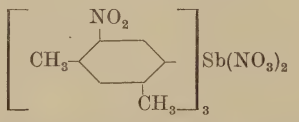
product on repeated crystallisation from aqueous alcohol melting at 161° C. When the dihydroxide in chloroform is warmed with concentrated hydrochloric acid, *tribenzylstibine dichloride*, M.pt. 108° C., is obtained. Nitration of the dihydroxide probably affords *trinitrotribenzylstibine dinitrate*, M.pt. 115° C., which yields *p*-nitrobenzoic acid on oxidation with 4 per cent. alkaline potassium permanganate solution.

Tri-5-nitrotri-m-xylylstibine oxide,[1]



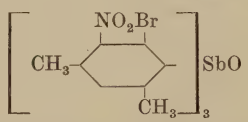
5 grams of the corresponding dinitrate are boiled for five hours with 300 c.c. of absolute alcohol containing 25 grams of phosphorous acid, and the resulting solution poured into 2 litres of water. The precipitated oxide (3·8 grams) is collected, dried, dissolved in chloroform and precipitated by light petroleum. It is a white crystalline powder, sintering at 210° C. and melting at 218° C., soluble in alcohol and giving an orange-coloured solution in chloroform. Solution of the oxide in glacial acetic acid and addition of ether causes the separation of *tri-5-nitrotri-m-xylylstibine diacetate*, $(C_8H_8.NO_2)_3Sb(OCOCH_3)_2$, a white precipitate, softening at 160° C. and melting at about 198° C.

Tri-5-nitrotri-m-xylylstibine dinitrate,



21 grams of tri-*m*-xylylstibine are slowly added to 100 c.c. of nitric acid (density 1·16), complete solution taking place, and the mixture, after being warmed for 20 minutes on the water-bath, is poured into 3 litres of water. The precipitate (38·2 grams) is collected after 15 minutes, dried and repeatedly recrystallised from alcohol. It is a white powder, sintering at 150° C. and melting at 175° C. with frothing. It is soluble in warm chloroform or acetic acid, slightly soluble in alcohol, insoluble in light petroleum. When heated with phosphorus pentabromide in chloroform solution at 130° C. for five hours, it gives a 65 per cent. yield of 4-bromo-6-nitro-*m*-xylene.

Tri-6-bromotri-5-nitrotri-m-xylylstibine oxide,

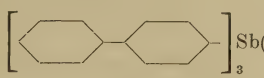


Tri-5-nitrotri-*m*-xylylstibine oxide in chloroform solution is treated with bromine in light petroleum. The product is a white, crystalline substance, melting at 162° C. to a yellow liquid, which decomposes with gas evolution at 168° C. When reduced in alcoholic ammonium hydroxide by zinc dust in the presence of ammonium chloride, the bromine is eliminated and tri-5-aminotri-*m*-xylylstibine obtained.

[1] Goddard, *Trans. Chem. Soc.*, 1923, 123, 2321.

Tri-α-naphthylstibine oxide, $(C_{10}H_7)_3SbO$,[1] is prepared by treating the dibromide or dichloride with alcoholic potassium hydroxide. It crystallises from carbon disulphide-benzene with one molecule of benzene, and melts at 219° to 220° C. The benzene may be removed by heating the product at 90° C. The oxide is slightly soluble in alcohol, moderately soluble in chloroform or carbon disulphide, sparingly soluble in ether, petroleum ether or benzene.

Tri-biphenylstibine dihydroxide,[2]



The corresponding halogen derivatives do not react with water, hot or cold, and only slowly with warm 95 per cent. ethyl alcohol. Boiling with alcohol containing ammonia for one hour, however, converts them quantitatively into *tri-biphenylstibine dihydroxide.* This separates from hot alcohol, in which it sparingly dissolves, as small, flat needles, commencing to sinter at 205° C. and melting with foaming at 210° to 211° C. It is almost insoluble in benzene.

Tri-biphenylstibine sulphide, $(C_6H_5.C_6H_4)_3SbS$, obtained by the action of hydrogen sulphide on an alcohol solution of the hydroxide, softens above 168° C. and melts with foaming at 173° C.

Compounds of the Types $ArAlk_2SbHal._2$ *and* $Ar_2AlkSbHal._2$.

Phenyldimethylstibine dichloride, $C_6H_5.Sb(CH_3)_2Cl_2$.—Phenyldimethylstibine is dissolved in 10 parts of carbon tetrachloride and treated with dry chlorine for 30 minutes. Spontaneous evaporation yields long, colourless prisms, which are treated with a little cold ether and recrystallised from acetic acid. The yield is quantitative. The product melts at 128° C., and is readily soluble in benzene.[3]

Phenyldimethylstibine dibromide, $C_6H_5.Sb(CH_3)_2Br_2$.—A dry solution of bromine in carbon tetrachloride is added to a similar solution of the stibine until a permanent bromine coloration persists. Evaporation of the solution at the ordinary temperature yields stout, colourless plates and prisms, M.pt. 112° to 113° C., possessing a similar solubility to the dichloride.

Phenyldimethylstibine di-iodide, $C_6H_5.Sb(CH_3)_2I_2$, occurs when a petroleum solution of iodine is added dropwise to a similar solution of the stibine. The di-iodide separates out immediately, and is a colourless, crystalline powder, M.pt. 98·5° to 99° C. Excess of iodine should be avoided or dark coloured by-products are produced.

Phenyldiethylstibine dichloride, $C_6H_5.Sb(C_2H_5)_2Cl_2$, is prepared similarly to the dimethyl compound. It is a colourless oil which cannot be distilled without decomposition. The *dibromide* has similar properties, but the *di-iodide* crystallises from benzene as pale yellow hexagonal plates, or long prisms from ether, M.pt. 88·5° to 89° C.

Diphenylmethylstibine dichloride, $CH_3.Sb(C_6H_5)_2Cl_2$, obtained by the direct action of chlorine on the stibine in carbon tetrachloride solution, separates from acetic acid as colourless prisms, M.pt. 144° C. The *dibromide* also crystallises as colourless prisms, M.pt. 148° C.

[1] Matsumiya, *Mem. Coll. Sci. Kyōtō*, 1925, **8**, 17.
[2] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2046.
[3] Grüttner and Wiernik, *Ber.*, 1915, **48**, 1759.

Diphenylethylstibine dichloride, $C_2H_5.Sb(C_6H_5)_2Cl_2$, prepared in the usual manner, separates from carbon tetrachloride as colourless plates, M.pt. 163° to 164° C., and the *dibromide* yields monoclinic plates, M.pt. 158° C.

Compounds of the Types $RSbX_2$ and RSbO.

The principal method of preparing the dihalogenated compounds $RSbX_2$, consists in heating the tertiary stibines for a prolonged period with antimony trichloride at a high temperature in an autoclave :

$$R_3Sb + SbX_3 = RSbX_2 + R_2SbX$$
$$R_2SbX + SbX_3 = 2RSbX_2$$

Some diaryl compound occurs as a by-product in the preparation.

Arylstibinoxides yield dihalides when their solutions in acetic acid are treated with halogen acids :

$$RSbO + 2HX = RSbX_2 + H_2O$$

A modification of this process consists in reducing arylstibinic acids and treating the reduced product with sodium halide in the presence of acid. The method is used for acids containing an amino-group substituted in the benzene nucleus, *e.g.* *m*-aminophenyldichlorostibine hydrochloride is formed when *m*-nitrophenylstibinic acid and stannous chloride are treated with a cold saturated solution of hydrogen chloride in alcohol. To transform this to the di-iodostibine hydriodide, its aqueous solution is acidified with hydrochloric acid and treated with a solution of sodium iodide.

Another method of preparation affords an interesting instance of degrading a secondary antimony compound to a primary compound, *e.g.* *p*-acetylaminophenyldichlorostibine hydrochloride occurs when di-*p*-acetylaminodiphenylstibinoxide in acetic acid is warmed for one hour on a water-bath at 70° C., then cooled in ice and treated with hydrochloric acid (density 1·17) at 0° C. The reaction takes twelve hours to complete, but only nine hours if the acetic acid is replaced by 100 per cent. formic acid :

$$[(CH_3.CO.NH.C_6H_4)_2Sb]_2O \longrightarrow 2CH_3.CO.NH.C_6H_4.SbO$$

The dichlorostibines containing an amino-group together with an hydroxyl or halogen grouping are prepared by the reduction of the corresponding nitro-acids.

All the dihalides are solids, the melting-points rising as the number and weight of the substituents in the benzene nucleus increases. Treatment of their alcoholic solutions with sodium sulphide or hydrogen sulphide converts them to sulphides. Chlorine readily adds on to yield tetrahalides, which are transformed by moisture to stibinic acids. *m*-Aminophenyldichlorostibine hydrochloride is slowly decomposed in aqueous solution yielding antimony trioxide and *m*-diaminodiphenylchlorostibine.

Oxides of the type RSbO are prepared by the following methods :—

(1) Arylstibinic acids in methyl alcohol containing hydrogen chloride are reduced by sulphur dioxide in the presence of iodine :

$$C_6H_5.SbO_2.nH_2O \xrightarrow[HI]{SO_2} C_6H_5.SbO$$

(2) An aqueous suspension of a dihalide is treated with aqueous sodium carbonate :

$$RSbCl_2 + Na_2CO_3 = RSbO + 2NaCl + CO_2$$

(3) Diarylstibinoxides in glacial acetic acid or 100 per cent. formic acid are degraded to monoaryl compounds when the mixture is heated in a carbon dioxide atmosphere ; the same result is attained in methyl alcohol-hydrogen chloride solution.

(4) Arylaminostibinoxides may be obtained by hydrolysis of the dichlorides by sodium or ammonium hydroxide, and also by the nitration of unsubstituted stibinic acids and subsequent reduction by tin and hydrochloric acid in the presence of acetic acid.

Phenylstibinoxide is the only unsubstituted oxide of its class known. Whilst it readily combines with acids, it is almost insoluble in alkali. Fuming nitric acid causes it to inflame, and hydrogen sulphide in the presence of ammonia converts it into the sulphide. If an amino-group is introduced into the nucleus the product becomes less stable and oxidises in the presence of alkali, tartaric acid increasing the rate of oxidation ; substitution in the amino-group, however, increases the stability. All the monoarylstibinoxides are solids.

Phenyldichlorostibine, $C_6H_5.SbCl_2$, may be prepared in two ways : (1) Triphenylstibine (30 grams) and 40 grams of antimony trichloride with 18 c.c. of xylene are heated together for 75 hours at 240° to 245° C.[1] The reaction takes place according to the equations :

$$(C_6H_5)_3Sb + SbCl_3 = C_6H_5.SbCl_2 + (C_6H_5)_2SbCl$$
$$(C_6H_5)_2SbCl + SbCl_3 = 2C_6H_5.SbCl_2$$

The dichloride forms about 70 per cent. of the crude organic product, the remainder being diphenylchlorostibine (see p. 215). (2) Phenylstibinoxide in 50 per cent. acetic acid is treated with 5*N* hydrochloric acid.[2]

The dichloride crystallises in shining needles or plates, M.pt. 62° C., B.pt. 290° C., readily soluble in alcohols, benzene, ether or light petroleum. It causes painful wounds on the skin and has a pungent irritating odour when warm. When the dry substance is heated on the water-bath, antimony trichloride is eliminated and diphenylchlorostibine produced. An alcoholic ammonia solution of the dichloride when saturated with hydrogen sulphide and acidified with hydrochloric acid yields phenylstibinous sulphide.[3]

Phenyldi-iodostibine, $C_6H_5.SbI_2$.[4]—The oxide in acetic acid solution is treated with hydrochloric acid and subsequently with concentrated sodium iodide solution, when the di-iodide is precipitated. It may also be obtained by reducing an ice-cold solution of phenylstibinic acid (10 grams) in 40 c.c. of hydrochloric acid (density 1·126) with 10 grams of stannous chloride in 30 c.c. of hydrochloric acid (density 1·126), and adding concentrated sodium iodide solution until precipitation is complete. The di-iodide crystallises from acetic acid

[1] Grüttner and Wiernik, *Ber.*, 1915, 48, 1749; see Morgan and Vining, *Trans. Chem. Soc.*, 1920, 117, 779; Morgan and Micklethwait, *ibid.*, 1911, 99, 2288; Hasenbäumer, *Ber.*, 1898, 31, 2912.

[2] Schmidt, *Annalen*, 1920, 421, 219; German Patent, 397458.

[3] Hasenbäumer, *loc. cit.*

[4] Schmidt, *loc. cit.*

in colourless needles, M.pt. 69° C., somewhat soluble in alcohols, acetone, carbon disulphide or ether. It is fairly stable in air when pure, but if impure it becomes red, antimony iodide separating out.

m - Aminophenyldichlorostibine hydrochloride,[1] $C_6H_4.NH_2.SbCl_2.HCl$.—*m*-Nitrophenylstibinic acid (30 grams) and 95 grams of stannous chloride are slowly treated with 230 c.c. of saturated alcoholic hydrogen chloride, the mixture being kept cool. The product separates, and is washed with concentrated hydrochloric acid and recrystallised from acidified methyl alcohol. It forms colourless needles, M.pt. 218° C. with decomposition.[2] It is fairly soluble in water and methyl alcohol, insoluble in acetone, benzene or ether. Its aqueous solution gradually decomposes, eliminating antimony trioxide and forming di-*m*-aminodiphenylchlorostibine, but the presence of hydrochloric acid somewhat checks the decomposition. When its aqueous solution is saturated with hydrogen sulphide, a sulphide may be precipitated by the addition of sodium acetate.

m-Aminophenyldi-iodostibine hydriodide, $C_6H_4.NH_2.SbI_2.HI$. —An aqueous solution of the chloride is acidified with hydrochloric acid, then treated with a solution of sodium iodide, the di-iodide separating as golden-yellow flocks. It melts at 160° C. to a dark red liquid, and is readily soluble in warm alcohol, sparingly soluble in water.

p-Aminophenyldichlorostibine hydrochloride is obtained by the method used for the *meta*-compound. It forms colourless crystals, M.pt. 122° to 125° C., readily soluble in methyl alcohol; its aqueous solution suffers more decomposition than that of the *meta*-derivative, which it resembles in properties.[3]

p-Acetylaminophenyldichlorostibine hydrochloride, $CH_3.CO.NH.C_6H_4.SbCl_2.HCl.H_2O$,[4] may be prepared in two ways: (1) *p*-Acetylaminophenylstibinic acid (50 grams) is stirred into 100 c.c. of ice-cold hydrochloric acid (density 1·19), 350 c.c. of glacial acetic acid added, followed by an ice-cold solution of 34 grams of stannous chloride in 150 c.c. of hydrochloric acid (density 1·19) containing a trace of iodine. After standing in ice for a few hours the product crystallises out; it is collected, washed with acetic acid-concentrated hydrochloric acid (1 : 1), then with ether, and dried. It forms colourless crystals, sintering at 125° C. It is not very stable and decomposes on keeping or on treating with ice-cold methyl alcohol into *p*-acetylaminophenyldichlorostibine, consisting of fine, colourless crystals, M.pt. 200° C., soluble in a large bulk of methyl alcohol. (2) 3 grams of di-*p*-acetylaminodiphenylstibinoxide are dissolved in 30 c.c. of acetic acid and warmed on the water-bath at 70° C. for one hour. The solution is cooled in ice and 60 c.c. of ice-cooled hydrochloric acid (density 1·17) added. After twelve hours 1·5 grams of hydrochloride are obtained, M.pt. 131° C. If the acetic acid be replaced by 100 per cent. formic acid, the reaction takes place at room temperatures in about nine hours.

3 - Amino - 4 - hydroxyphenyldichlorostibine hydrochloride, $(C_6H_3.OH.NH_2)SbCl_2.HCl$.—To a solution of 60 grams of stannous chloride in 45 c.c. of saturated alcoholic hydrogen chloride maintained at −5° C., a solution of 24 grams of 3-nitro-4-hydroxyphenylstibinic acid

[1] Compare Schmidt and Hofmann, *Ber.*, 1926, 59, [B], 555.
[2] Compare German Patent, 268541.
[3] Schmidt and Hofmann, *loc. cit.*
[4] Schmidt, *Annalen*, 1922, 429, 129.

in 60 c.c. of the same solvent is gradually added. When the temperature has risen to 22° C. the mixture is placed in ice for two days, when the hydrochloride is slowly deposited. It is collected, washed with cold concentrated hydrochloric acid, dried, dissolved in methyl alcohol and re-precipitated by ether. It melts with decomposition at 165° to 170° C., and is converted to the oxide by cold ammonium hydroxide, and to the stibinic acid by hydrogen peroxide in alkaline solution.

3 - Amino - 4 - chlorophenyldichlorostibine hydrochloride, $(C_6H_3.NH_2.Cl)SbCl_2.HCl$,[1] occurs when 3-nitro-4-chlorophenylstibinic acid and stannous chloride are treated gradually with alcoholic hydrogen chloride. It forms white needles, M.pt. 153° C. with decomposition, readily soluble in methyl alcohol, the solution yielding *3-amino-4-chlorophenylstibinoxide* as a voluminous precipitate when treated with dilute ammonium hydroxide. This oxide is more stable than the unchlorinated oxide; it is converted to the dichloride by concentrated hydrochloric acid and to a *sulphate* by dilute sulphuric acid.

Phenylstibinoxide, $C_6H_5.SbO$, may be prepared in several ways: (1) 25 grams of phenylstibinic acid in 100 c.c. of hydrochloric acid (density 1·18) are diluted with 200 c.c. of methyl alcohol and 90 c.c. of water. The mixture is cooled in ice, 0·5 gram of sodium iodide added and the liquid then saturated with sulphur dioxide. After several hours the whole is poured upon ice, and the oxide filtered off, washed and dried.[2] (2) Diphenylstibinoxide is boiled for 20 minutes in glacial acetic acid solution in an atmosphere of carbon dioxide, and the mixture afterwards cooled and treated with ice-cold ammonium hydroxide to precipitate the required oxide. This change also takes place when diphenylstibinoxide is warmed with 100 per cent. formic acid at 70° C. Another modification of the process is as follows: 3 grams of diphenylstibinoxide in 30 c.c. of methyl alcohol and 14 c.c. of saturated alcoholic hydrogen chloride are boiled in a carbon dioxide atmosphere for 4·5 hours. After cooling the mixture is stirred into ice-cold sodium hydroxide, when the impure monoaryl oxide separates. The latter is filtered off, dissolved in ammoniacal hydrogen peroxide, the solution filtered, and the oxide again precipitated by acidification with hydrochloric acid.[3] (3) Phenyldichlorostibine in aqueous suspension is treated with aqueous sodium carbonate.[4]

The oxide is a white voluminous powder, sintering at 153° to 154° C., readily soluble in acetic or formic acid, but insoluble in most organic solvents. It is practically insoluble in alkali, but combines with halogen acids. Nitric acid (density 1·49) causes it to inflame. When the oxide in alcoholic ammonia is saturated with hydrogen sulphide, acidification of the solution with hydrochloric acid precipitates *phenylstibinous sulphide*, $C_6H_5.SbS$, which may be recrystallised from alcohol, and melts at 65° C. Phenyldichlorostibine yields the sulphide under similar conditions.

m-Aminophenylstibinoxide, $NH_2.C_6H_4.SbO$.—*m*-Aminophenyldichlorostibine hydrochloride yields this oxide when hydrolysed by aqueous sodium hydroxide[5] or better by ammonium hydroxide.[6] It

[1] Schmidt, *Annalen*, 1920, **421**, 231; compare Schmidt and Hofmann, *Ber.*, 1926, 59, [B], 555.
[2] Schmidt, *Annalen*, 1920, **421**, 217.
[3] Schmidt, *Annalen*, 1922, **429**, 143.
[4] Hasenbäumer, *Ber.*, 1898, **31**, 2912.
[5] German Patent, 268451.
[6] Schmidt, *Annalen*, 1920, **421**, 225.

may also be obtained by nitrating phenylstibinic acid and reducing the *m*-nitro-acid obtained by tin and hydrochloric acid containing a little glacial acetic acid.[1] The oxide is an amorphous colourless powder, sintering at about 170° C., easily soluble in dilute acids, and from sulphuric acid solution alcohol precipitates a sulphate. In alcohol it is sparingly soluble, but it may be dissolved in a large bulk of methyl alcohol. Treatment with dilute alkaline hydrogen peroxide, followed by hydrochloric acid, precipitates a substance which probably has the constitution $HCl.NH_2.C_6H_4.SbOCl_2$. The oxide tends to oxidise further in the presence of alkali, and if tartaric acid also be present the rate of oxidation increases. It appears to exist also in a hydrated form, and the antimony content therefore varies in different preparations.

p-Acetylaminophenylstibinoxide, $CH_3.CO.NH.C_6H_4.SbO.H_2O$,[2] occurs when *p*-acetylaminophenyldichlorostibine hydrochloride in ice-cold methyl alcohol is treated with normal ammonium hydroxide. It is an amorphous powder, sintering at about 180° C., slightly soluble in methyl alcohol or acetic acid, and when freshly precipitated dissolves in water, especially in the presence of sodium hydroxide.

p-Tolyldichlorostibine, $CH_3.C_6H_4.SbCl_2$.[3]—Tri-*p*-tolylstibine (10 grams) and 12 grams of antimony trichloride in xylene solution are heated together for 48 hours at 245° C. The reaction mixture is then distilled in carbon dioxide, the dichloride being obtained as a crystalline solid, M.pt. 93·5° C., B.pt. above 360° C. It yields a tetrachloride, oxide and sulphide.

Mono-biphenyldichlorostibine,[4]

A mixture of 10 grams of tri-biphenylstibine and 8 grams of antimony trichloride in 25 c.c. of xylene is heated at 220° to 240° C. in a sealed tube for 100 hours. The pasty product is filtered by suction and washed with cold benzene, about 9·6 grams resulting. The black filtrate contains an appreciable amount of diphenyl, and is a mixture of two substances difficult to separate. It is dissolved in hot benzene and filtered while warm, the filtrate depositing crystals on standing, which are removed and the new filtrate concentrated until a new crop of crystals forms. Each crop is dissolved in warm benzene and the process repeated a number of times. Eventually the mixture is separated into two portions, the less soluble portion consisting of needle-like crystals and the main part of lustrous plates. Slightly more than 0·5 gram of di-biphenylchlorostibine and 2 grams of mono-biphenyldichlorostibine are isolated. The latter forms lustrous white plates from benzene, melting with previous sintering at 132° to 133° C. The vapours of the hot substance are irritating to the throat, while the skin of the face is slightly sensitive to the solid itself.

Mono-biphenylstibinoxide, $C_6H_5.C_6H_4.SbO$, is prepared from the dichloride by the action of alcoholic ammonia. It softens above 155° C., melting slowly at 159° to 160° C.

[1] May, *Trans. Chem. Soc.*, 1912, 101, 1033; German Patent, 268451.
[2] Schmidt, *Annalen*, 1922, 429, 130.
[3] Hasenbäumer, *Ber.*, 1898, 31, 2914.
[4] Worrall, *J. Amer. Chem. Soc.*, 1930, 52, 2046.

Compounds of the Types R_2SbX and $(R_2Sb)_2O$.

Unlike the secondary arsines, only derivatives of secondary stibines are known, the parent products R_2SbH not having been described to date. The halides are prepared by indirect means by the following methods :—

(1) Triarylstibines are heated with antimony trichloride in an autoclave at a high temperature for a prolonged period :

$$R_3Sb + SbCl_3 = R_2SbCl + RSbCl_2$$

(2) Triacetamidotriarylstibines in ice-cooled methyl alcohol are treated with alcoholic hydrogen chloride, diacetamidodiarylchlorostibine hydrochlorides being obtained.

(3) Arylaminodichlorostibine hydrochlorides are boiled with water, the antimony trioxide removed, and hydrochloric acid added.

(4) Triarylstibine dihalides when heated under reduced pressure (5 to 7 mm.) eliminate aryl halide :

$$R_3SbX_2 = R_2SbX + RX$$

All the halogen compounds of the type R_2SbX are solid and fairly stable, the stability decreasing in the presence of substituted amino-groups. The chlorides combine with chlorine yielding diarylstibinic chlorides, R_2SbCl_3, which on hydrolysis give diarylstibinic acids.

The diarylstibinoxides, $(R_2Sb)_2O$, have been isolated in a variety of ways, the investigation up to the present having been confined to phenyl compounds and their amino-substitution products :

(1) A triarylstibine in methyl alcohol containing hydrogen chloride is boiled under reflux in a carbon dioxide atmosphere, then treated with dilute ammonium or sodium hydroxide.

(2) A dry monoarylstibinoxide is heated at 100° C. in an atmosphere of carbon dioxide :

$$4RSbO = (R_2Sb)_2O + Sb_2O_3$$

(3) A monoarylstibinoxide in acetic acid containing 20 per cent. tartaric acid is allowed to stand for a long period, the resulting product dissolved in methyl alcohol and treated with dilute ammonium hydroxide.

(4) Diarylchlorostibines are digested with aqueous sodium carbonate.

(5) Diaminodiarylstibinic acids in methyl alcohol solution are reduced by sulphur dioxide at a temperature not exceeding 25° C., and, after treatment with warm hydrochloric acid and dilution, the mixture is filtered and sodium hydroxide added in the presence of ice.

(6) Diaminodiarylstibinous hydroxides are isolated by reducing the corresponding dinitrodiarylstibinic acids by tin and hydrochloric acid or zinc dust and ammonium chloride.

The secondary arylstibinoxides are solids which do not possess very definite melting-points. Treatment with acids yields the corresponding salts, and hydrogen sulphide converts them into the corresponding sulphides. Diphenylstibinoxide is reduced by hypophosphorous acid to tetraphenyldistibine.

Diphenylchlorostibine, $(C_6H_5)_2SbCl$, occurs to the extent of about 30 per cent. when triphenylstibine and antimony trichloride are heated together in xylene solution at 250° to 280° C. in the proportions given

under phenylstibine dichloride (p. 211). The higher-boiling fraction obtained when the reaction mixture is distilled under reduced pressure contains the diphenylchlorostibine.[1] The reaction is best carried out in the rotating autoclave about to be described.[2]

The rotating autoclave shown is a vessel formed by boring out the steel core of a 6-inch high-explosive shell until the thickness of the wall was about 1·9 cm. The steel cover, which is of similar thickness, is fastened down with twelve bolts and rendered gas-tight with a lead washer. The cover carries a powerful adjustable spring safety-valve, a steel thermometer tube projecting into the cavity of the autoclave, and a hollow steel tube carrying an all-steel pressure gauge, which communicates with the interior of the vessel by means of a narrow-bored steel tube dipping into and protected by a concentric steel case partly filled with heavy oil, and having a small aperture at its upper end for admitting the compressed gases from the autoclave. The pressure-gauge tube is fixed in the centre of the cover and fitted with a pulley, so that it also serves as the axle of rotation for the autoclave, which is supported and spun in an inclined position. The vessel used in the foregoing preparation had a working capacity of 1 litre. A glass lining blown to fit into the cavity of the autoclave was employed in lieu of an enamelled lining.

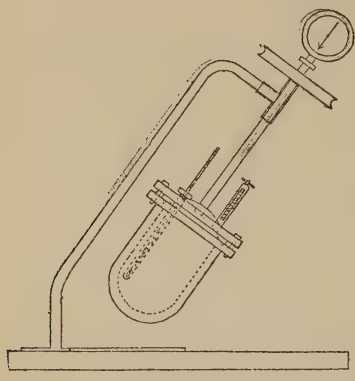


Fig. 5.

The compound forms white crystals, M.pt. 68° C., soluble in alcohol, ether or benzene, insoluble in water and not hydrolysed by this solvent. It combines directly with chlorine, yielding diphenylstibinic chloride.

Di-m-aminodiphenylchlorostibine dihydrochloride, $(C_6H_4.NH_2.HCl)_2SbCl$.[3]—8 grams of *m*-aminophenyldichlorostibine hydrochloride are boiled for one hour with 500 c.c. of water, antimony trioxide separating out. The latter is removed, the filtrate evaporated and the residue taken up in a little water. After again filtering, hydrochloric acid is added, the dihydrochloride separating as colourless needles (3·7 grams), M.pt. 215° C. with decomposition.[4] It readily dissolves in water, and alkali precipitates the hydroxide.

Di-p-acetylaminodiphenylchlorostibine hydrochloride, $(CH_3.CO.NH.C_6H_4)_2SbCl.HCl$.[5]—4 grams of tri-*p*-acetylaminotriphenylstibine (M.pt. 205° C.) are suspended in a little methyl alcohol, cooled in ice, and alcoholic hydrogen chloride added in excess. Fine crystals slowly separate and are collected after several hours, washed with dilute alcoholic hydrogen chloride and dried. 3 grams of substance are

[1] Grüttner and Wiernik, *Ber.*, 1915, 48, 1749; see May, *Trans. Chem. Soc.*, 1912, 101, 1033; Morgan and Micklethwait, *ibid.*, 1911, 99, 2286; Michaelis and Günther, *Ber.*, 1911, 44, 2318; Hasenbäumer, *ibid.*, 1898, 31, 2910; Michaelis and Reese, *Annalen*, 1886, 233, 57.

[2] Morgan and Vining, *Trans. Chem. Soc.*, 1920, 117, 777.

[3] Schmidt, *Annalen*, 1920, 421, 239.

[4] See Morgan and Micklethwait, *Trans. Chem. Soc.*, 1911, 99, 2296; *Proc. Chem. Soc.*, 1912, 28, 20.

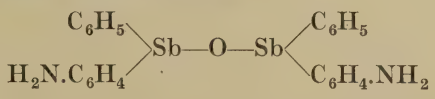
[5] Schmidt, *Annalen*, 1922, 429, 136.

obtained, M.pt. about 135° C., soluble in a large bulk of methyl alcohol. The product is not stable, the hydrochloric acid present slowly hydrolysing the acetyl group even in closed vessels.[1] The corresponding *bromo-hydrobromide* is obtained in a similar manner.

Diphenylstibinoxide, $[(C_6H_5)_2Sb]_2O$, may be prepared in several ways: (1) Triphenylstibine (9 grams) with 150 c.c. of methyl alcohol and 30 c.c. of saturated alcoholic hydrogen chloride is boiled for one hour under reflux in a stream of carbon dioxide. The whole is then cooled in ice and treated with an excess of dilute sodium hydroxide, when a milky separation of oxide occurs. This is extracted with ether, the aqueous alcohol solution containing a little diphenylstibinic acid. Evaporation away of the ether gives a good yield of the oxide as an oil, which is crystallised from alcohol.[2] (2) Dry phenylstibinoxide is heated on a boiling water-bath in a carbon dioxide atmosphere for four hours. The product is then extracted with warm alcohol to remove antimony trioxide, slow evaporation of the extract yielding thick shining crystals of the oxide.[3] (3) 5 grams of phenylstibinoxide in 50 c.c. of acetic acid are treated with 25 c.c. of 20 per cent. tartaric acid. After long standing, crystals separate, M.pt. 132° C., which appear to be the tartrate. These are dissolved in methyl alcohol and dilute ammonium hydroxide stirred in, a milky precipitate of the oxide separating and slowly solidifying. (4) Diphenylchlorostibine is digested with aqueous sodium carbonate.[4]

The oxide forms colourless crystals, M.pt. 78° to 80° C. When dissolved in acetic acid and treated with hydrochloric acid (density 1·18), it yields diphenylchlorostibine, M.pt. 68° C. It is reduced by hypophosphorous acid to tetraphenyldistibine, $(C_6H_5)_2Sb.Sb(C_6H_5)_2$, a yellow compound. Nitric acid reacts violently with the oxide. Hydrogen peroxide in alkaline-alcoholic solution converts it to diphenylstibinic acid.

m-Diaminodiphenylstibinoxide,[5]



The hydrochloride from *m*-diaminodiphenylstibinic acid (43 parts) is dissolved in 300 parts of warm methyl alcohol, the solution cooled and saturated with sulphur dioxide at a temperature not exceeding 25° C. After standing for some hours, 20 parts of hydrochloric acid (density 1·123) followed by 100 parts of water are added and the mixture filtered from by-products. The oxide is precipitated from the filtrate by rendering it alkaline with sodium hydroxide in the presence of ice. The product is a slightly coloured powder, sintering at about 70° C., and having an irritant action on the mucous membrane of the nose. It reduces Tollen's reagent and is insoluble in alkali.

Di-m-aminodiphenylstibinous hydroxide, $(C_6H_4.NH_2)_2SbOH$,[6] occurs when the corresponding stibinous chloride hydrochloride in

[1] Compare German Patent, 397079.
[2] Schmidt, *loc. cit.*
[3] Schmidt, *Annalen*, 1920, 421, 234; German Patent, 389151.
[4] Michaelis and Günther, *Ber.*, 1911, 44, 2318.
[5] German Patent, 269206.
[6] Schmidt, *loc. cit.*; see Morgan and Micklethwait, *Proc. Chem. Soc.*, 1912, 28, 20.

aqueous solution is treated with alkali, or by reducing 3 : 3′-dinitrodiphenylstibinic acid with tin and hydrochloric acid or zinc and ammonium chloride. It is a caseous, colourless precipitate, soon becoming hard. It sinters above 70° C., and is soluble in alcohol or acetone, sparingly soluble in ethyl acetate.

Di-p-acetylaminodiphenylstibinous hydroxide, $(CH_3.CO.NH.C_6H_4)_2SbOH.1{\cdot}5H_2O$.[1]—Di-*p*-acetylaminodiphenylchlorostibine hydrochloride suspended in methyl alcohol is treated with 5*N* sodium hydroxide solution until the mixture is alkaline. Water is added until a permanent turbidity occurs, the mixture filtered and placed in ice, when the hydroxide separates. It forms small, colourless crystals, melting at about 130° C., fairly soluble in methyl alcohol, sparingly soluble in ethyl alcohol. A more recent method of preparation [2] consists of boiling a suspension of di-*p*-acetamidodiphenylchlorostibine hydrochloride (10 grams) in 1000 c.c. of 0·005*N* sodium hydroxide solution for one hour. The product intumesces at 128° C. In acetic or formic acid solution the hydroxide decomposes with formation of *p*-acetylaminostibinoxide.

Diphenylstibinous acetate, $(C_6H_5)_2SbO.CO.CH_3$.—When diphenylstibinoxide is dissolved in a little hot glacial acetic acid and the solution cooled, the acetate crystallises as shining, colourless needles, M.pt. 132° C., readily soluble in warm methyl alcohol, hydrolysed by water.

Diphenylstibinous sulphide, $[(C_6H_5)_2Sb]_2S$.[3]—The oxide in alcoholic solution is treated with hydrogen sulphide and the solution evaporated. The sulphide forms long white needles, M.pt. 69° C.

Di-p-tolylchlorostibine, $(CH_3.C_6H_4)_2SbCl$.[4]—Tri-*p*-tolylstibine dichloride (2 grams) is heated under 5 to 7 mm. pressure, *p*-chlorotoluene distilling at 60° to 65° C. and the chlorostibine at 160° to 200° C. in almost quantitative yield. After washing with light petroleum and alcohol the stibine is obtained as a white solid.

Di-p-tolylbromostibine, $(CH_3.C_6H_4)_2SbBr$, is obtained in a similar manner to the chloro-compound. It is a pale cream substance, M.pt. above 290° C., sparingly soluble in organic solvents.

Di-p-tolyliodostibine, $(CH_3.C_6H_4)_2SbI$, is a white solid, M.pt. 233° C., almost insoluble in cold organic solvents, but soluble on warming.

Di-biphenylchlorostibine,[5] $(C_6H_5.C_6H_4)_2SbCl$, may be obtained as described under mono-biphenyldichlorostibine (p. 214) or by heating tri-biphenylstibine dichloride above its melting-point. The yield by the latter process is very small, since decomposition occurs, a good yield of 4-chlorodiphenyl resulting. The chlorostibine separates from benzene in aggregates of small needles, softening gradually above 150° C., and melting at 187° to 188° C.

Di-biphenylstibinoxide, $[(C_6H_5.C_6H_4)_2Sb]_2O$, is a white, crystalline powder, melting at 120° to 121° C. with previous sintering, and obtained from the foregoing chloride by the action of alcoholic ammonia.

[1] Schmidt, *Annalen*, 1922, **429**, 137.
[2] Morgan and Cook, *J. Chem. Soc.*, 1930, p. 741.
[3] Michaelis and Günther, *loc. cit.*
[4] Goddard and Yarsley, *Trans. Chem. Soc.*, 1928, p. 720.
[5] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2046.

Compounds of the Types $RSbCl_4$ and R_2SbCl_3.

The tetrachlorides, $RSbCl_4$, were amongst some of the earliest aromatic antimonials obtained, owing to the fact that they are simple chlorine addition products of the aryldichlorostibines. The methods of preparation are as follows :—

(1) By the further chlorination of compounds of the type $RSbCl_2$:

$$RSbCl_2 + Cl_2 = RSbCl_4$$

(2) By the action of concentrated hydrochloric acid upon arylstibinic acids.

The compounds are decomposed by water, yielding arylstibinic acids, and are solids melting with decomposition. When arylstibinic acids in concentrated hydrochloric acid are treated with aqueous ammonium chloride solution saturated with hydrogen chloride, double salts of the type $(RSbCl_5)NH_4$ are produced, associated with varying amounts of water. Such compounds are hydrolysed by water to arylstibinic acids. Similar types of salts are obtained with aniline and similar amines, also with pyridine and quinoline.

The trichlorides, R_2SbCl_3, are isolated by the following methods :—

(1) Diarylchlorostibines are treated with dry chlorine :

$$R_2SbCl + Cl_2 = R_2SbCl_3$$

(2) By treating diarylstibinic acids with concentrated hydrochloric acid.

(3) The type R_2SbCl_3 occurs as a by-product, together with the triarylstibine dichloride, when triarylstibines are prepared by the Fittig reaction.

(4) Triarylstibines in acetone are treated with a boiling mixture of water and $5N$ sodium hydroxide solution, followed by 6 per cent. hydrogen peroxide. The precipitate then formed by the addition of dilute sulphuric acid is converted to the trichloride by hydrochloric acid.

The diarylstibinic chlorides are susceptible to moisture, being hydrolysed to diarylstibinic acids.

Phenylstibinic chloride, $C_6H_5.SbCl_4$, may be obtained by saturating a cold ether solution of phenyldichlorostibine with chlorine and evaporating the solution,[1] or by treating phenylstibinic acid with concentrated hydrochloric acid and evaporating the solution on the water-bath.[2] It forms very hygroscopic crystals, M.pt. 60° to 65° C., easily soluble in ether, benzene, hot chloroform or hydrochloric acid. It is hydrolysed to the stibinic acid by water, and gradually decomposes on keeping or rapid heating, yielding diphenylstibinic chloride and antimony trichloride.

When a hydrochloric acid solution of phenylstibinic acid is treated with a saturated hydrochloric acid solution of ammonium chloride, a yellow precipitate of *ammonium phenyl chloroantimonate* separates. This is washed free from ammonium chloride by concentrated hydrochloric acid and dried. It is a pale yellow voluminous powder, M.pt. above 260° C., stable in air and decomposed by water, yielding phenylstibinic acid. It has the constitution $(C_6H_5.SbCl_5)NH_4$, and similar salts may be obtained with aniline, dimethylaniline, pyridine, quinoline,

[1] Hasenbäumer, *Ber.*, 1898, 31, 2913.
[2] Schmidt, *Annalen*, 1920, 421, 199.

dicyandiamidine and guanidine; urea gives a colourless precipitate, ethylamine and allylamine faint yellow precipitates, methylamine a colourless precipitate soon becoming yellow, and urethane an oil.

o-Nitrophenylstibinic chloride, $NO_2.C_6H_4.SbCl_4$.—*o*-Nitrophenylstibinic acid in methyl alcohol is treated with concentrated hydrochloric acid, the oil which separates soon solidifying to crystalline plates. These melt at 127° C., and are easily soluble in alcohol or ether. The chloride is slowly decomposed by water, which precipitates yellow flocks of the stibinic acid from alcoholic solution.

m-Nitrophenylstibinic chloride, $NO_2.C_6H_4.SbCl_4.H_2O$, crystallises from a solution of *m*-nitrophenylstibinic acid in warm hydrochloric acid (density 1·18). It sinters at about 60° C., and when kept in a vacuum desiccator for 14 days the melting-point rises to about 140° C. It is fairly soluble in ether or alcohol, and with water yields the stibinic acid. The *ammonium double salt*, $(NO_2.C_6H_4.SbCl_5)NH_4.\frac{1}{3}H_2O$, prepared in the same way as the corresponding phenyl compound, sinters above 235° C.

m-Aminophenylstibinic chloride hydrochloride, $(NH_2.HCl)C_6H_4.SbCl_4.1\frac{1}{2}H_2O$, occurs when *m*-aminophenylstibinic acid is treated with concentrated hydrochloric acid. It forms colourless crystals, blackening above 190° C., readily soluble in water or alcohol.

p-Aminophenylstibinic chloride hydrochloride, $(NH_2.HCl)C_6H_4.SbCl_4.1\frac{1}{2}H_2O$, is prepared by stirring a moist paste of *p*-aminophenylstibinic acid with ice-cooled hydrochloric acid (density 1·19). It is a pale yellow powder, melting with decomposition at about 155° C., readily soluble in water or alcohol. When heated for half an hour on the water-bath in dilute aqueous solution, most of the antimony is eliminated, but this change does not take place with *m*-aminophenylstibinic acid.[1]

p-Chlorophenylstibinic chloride, $ClC_6H_4.SbCl_4$,[2] is a yellow, crystalline substance, deliquescent in air. When *p*-chlorophenylstibinic acid in concentrated hydrochloric acid (density 1·126) is treated with a saturated solution of ammonium chloride in hydrochloric acid, a citron-yellow precipitate of *ammonium p-chlorophenyl chloroantimonate*, $(ClC_6H_4.SbCl_5)NH_4.\frac{1}{3}H_2O$, is obtained. This is unchanged at 250° C., forms a colourless solution in methyl alcohol and is hydrolysed by water.

m-Nitro-p-chlorophenylstibinic chloride, $NO_2.Cl.C_6H_3.SbCl_4.5H_2O$, obtained in the usual way, forms colourless crystals which melt at 80° C. when dried in air. It is fairly soluble in ether, readily soluble in warm chloroform, insoluble in benzene, and hydrolysed by water. When the pentahydrate is dried in a vacuum, four molecules of water are driven off, the resulting *monohydrate* sintering at 122° C. The *double salt* with *ammonium chloride* is a colourless compound having the composition $(NO_2.Cl.C_6H_3.SbCl_4)_2NH_3.8H_2O$. It is soluble in alcohols and ether, decomposed by water, and unmelted up to 220° C.

Diphenylstibinic chloride, $(C_6H_5)_2SbCl_3.H_2O$, may be prepared in several ways: (1) It crystallises out when a hot solution of diphenylstibinic acid in dilute hydrochloric acid is cooled.[3] (2) Antimony trichloride (48 grams) and 48 grams of chlorobenzene are dissolved in 150 to 200 c.c. of dry benzene and added to 20 grams of sodium which has

[1] Schmidt, *Annalen*, 1922, 429, 146.
[2] Schmidt, *Annalen*, 1920, 421, 207.
[3] Schmidt, *Annalen*, 1920, 421, 236.

been granulated under toluene. If the reaction does not start spontaneously, the mixture is gently warmed. After 24 hours the mixture is filtered, the filtrate evaporated and the residual oil triturated with alcoholic hydrochloric acid until it solidifies, the solid then being dissolved in the minimum quantity of boiling alcohol. On cooling, most of the triphenylstibine dichloride crystallises out, and concentration of the mother liquors yields impure diphenylstibinic chloride. This is purified by extraction with hot dilute hydrochloric acid, the acid solution when filtered from triphenylstibine dichloride giving colourless crystals of the required chloride. The yield varies from 11 to 16 per cent. on the weight of antimony trichloride.[1] (3) Diphenylchlorostibine is treated with dry chlorine and the resulting product recrystallised from dilute hydrochloric acid.[2] (4) It occurs as a by-product when mercury diphenyl and antimony trichloride are heated together in a sealed tube in xylene solution at 130° C.[3]

The chloride crystallises in needles, M.pt. 176° C., soluble in alcohol or dilute hydrochloric acid, insoluble in water. Alcoholic silver nitrate converts it into a *basic nitrate*, consisting of colourless needles, decomposing at 206° C.

mm′-Diaminodiphenylstibinic chloride dihydrochloride, $(C_6H_4.NH_2)_2SbCl_3.2HCl.2H_2O$, is obtained as a fine, crystalline precipitate, obtained when an excess of hydrochloric acid is added to *mm′*-diaminodiphenylstibinic acid. It does not melt at 250° C. and dissolves only slowly in cold water, more readily on heating.

Di-p-tolylstibinic chloride, $(C_6H_4.CH_3)_2SbCl_3$.—A solution of 6 grams of tri-*p*-tolylstibine in acetone is gradually added to a boiling mixture of 113 c.c. of water, 37 c.c. of 5*N* sodium hydroxide and 22·5 c.c. of 6 per cent. hydrogen peroxide. Any precipitate which is formed is removed and dilute sulphuric acid added. The white voluminous precipitate which results is reprecipitated, first from 5*N* hydrochloric acid as the *pyridine double salt* and then from dilute sodium hydroxide by means of dilute acetic acid. It is then dissolved in moderately concentrated boiling hydrochloric acid and the solution evaporated to small bulk. Colourless needles of the trichloride separate, which crystallise from benzene as colourless plates, sintering at 130° C. and melting at 141° to 142° C.[4]

3 : 3′ : 5 : 5′-Tetrachloro-4 : 4′-dianisylstibinic chloride, $(CH_3O.C_6H_2Cl_2)_2SbCl_3$.[5]—Chlorine is passed into one part of tri-*p*-anisylstibine in fifteen parts of dry chloroform. The solvent is removed and the residue dissolved in benzene, from which the trichloride slowly separates. The whole operation must be conducted in a dry atmosphere owing to the susceptibility of the product to moisture. The chloride forms colourless crystals, M.pt. 184° C., readily soluble in chloroform or ether, sparingly soluble in alcohol or benzene, insoluble in light petroleum.

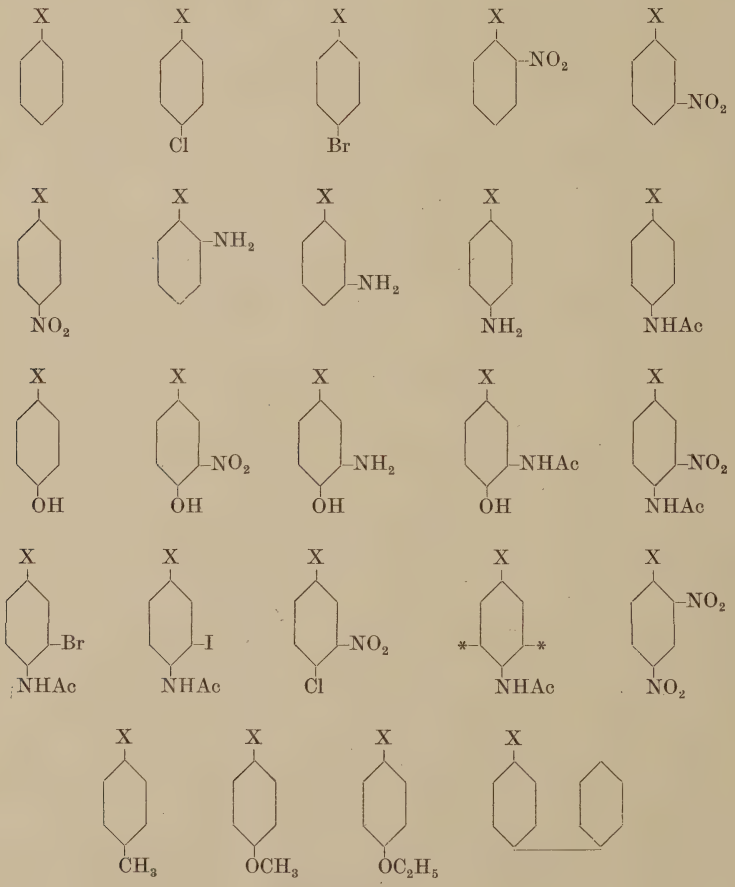
Di-biphenylstibinic chloride,[6] $(C_6H_5.C_6H_4)_2SbCl_3$, isolated by the action of chlorine on di-biphenylchlorostibine in chloroform solution,

[1] Morgan and Micklethwait, *Trans. Chem. Soc.*, 1911, 99, 2286; see Michaelis and Reese, *Annalen*, 1886, 233, 58.
[2] Michaelis and Günther, *Ber.*, 1911, 44, 2319.
[3] Hasenbäumer, *Ber.*, 1898, 31, 2911.
[4] Goddard and Yarsley, *J. Chem. Soc.*, 1928, p. 719.
[5] Löloff, *Ber.*, 1897, 30, 2834.
[6] Worrall, *J. Amer. Chem. Soc.*, 1930, 52, 2046.

forms pale yellow flat needles, softening above 200° C. and melting at 210° C.

Primary Arylstibinic Acids.

The production of many of the compounds under this heading has been made possible only owing to the discovery that antimony can be introduced into the benzene ring by use of the diazo-reaction. The older method consisted in the hydrolysis of arylstibinic chlorides, but to obtain the latter it is first necessary to prepare the triarylstibine and subject it to " dearylation." This process, apart from being long and tedious, does not give particularly good or consistent yields. The following scheme shows the main primary arylstibinic acids known (excluding condensation products), X denoting the grouping $-SbO(OH)_2$.



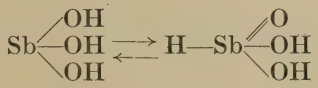
The preparation of these derivatives may be accomplished as follows :—

(1) By the hydrolysis of arylstibinic chlorides :

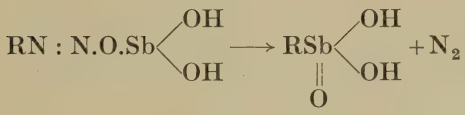
$$RSbCl_2 \longrightarrow RSbCl_4 \longrightarrow RSbO(OH)_2$$

(2) Monoaryldichlorostibines in alkaline solution are treated with hydrogen peroxide.

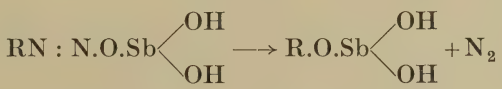
(3) By the use of the diazo-reaction. In this connection Schmidt [1] considers that antimony trioxide must act as antimonious acid when taking part in this reaction and may exist in tautomeric forms as shown by



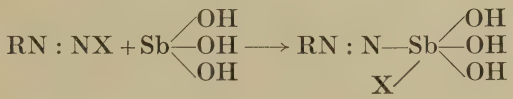
If the reaction between the diazo-compound and the antimony oxide took the normal course as in the case of arsenious oxide,[2] the following scheme would represent the formation of arylstibinic acids :

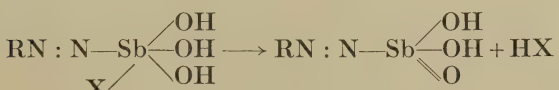


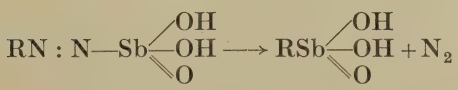
It is possible to have another representation of the last phase of this reaction :



but this may be ruled out as untenable since the resulting product would be an ester of antimonious acid, and such products are not stable in the presence of water.[3] Supposing that the antimony changes to the pentavalent condition during the reaction, the scheme might be represented in the following manner : [4]



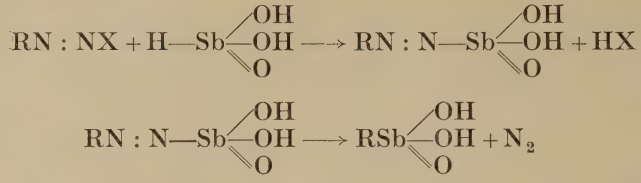




According to this representation a diazostibinic acid is produced, simple evolution of nitrogen then giving the stibinic acid. Such a

[1] Schmidt, *Annalen*, 1920, 421, 174.
[2] See this Vol., Part II, pp. 154, 155.
[3] Mackey, *Trans. Chem. Soc.*, 1909, 95, 604.
[4] Compare Christiansen, "Organic Derivatives of Antimony," *Chem. Catalog. Co.*, 1925, pp. 56, 57.

product would also be obtained if the tautomeric form of the antimonious acid is involved :



As is often the case when using the diazo-reaction, each compound requires its own special conditions of preparation, and acid, neutral or alkaline, media are employed to suit the specific case under investigation, and occasionally a catalyst is beneficial for facilitating the evolution of the diazo-nitrogen. The antimony is sometimes introduced in the form of tartar emetic, or double compounds of aryl diazonium chlorides with antimony trichloride may be treated with sodium hydroxide. A variation of the latter procedure consists of mixing the amine in hydrochloric acid with antimony trichloride in the same solution, diazotising the mixture, then rendering it alkaline. Nitroarylstibinic acids are prepared by diazotisation of nitroarylamines or direct nitration of arylstibinic acids, when the nitro-group enters the ring in the *meta*-position to the antimony. Reduction of the nitro-acids by ferrous hydroxide or titanous chloride yields the corresponding aminoarylstibinic acids. The latter may be acetylated, diazotised or condensed with such substances as ethyl chlorocarbonate or benzene sulphonic chloride in the usual manner. The acids $RSbO(OH)_2$ are usually amorphous products, having no melting-point. They dissolve in alkalis, but are insoluble in water ; they yield salts with the heavy metals. They are amphoteric, dissolving in concentrated hydrochloric acid to afford arylstibinic chlorides. Reduction may lead to stibinous oxides or stibino-compounds, the ultimate product depending upon the reducing agent employed.

The formulæ assigned to the arylstibinic acids have given rise to considerable discussion. This is due to the fact that the products may be isolated with varying degrees of water of hydration, the amount depending upon the method of preparation and the conditions of drying the acids. Those which are formed by the hydrolysis of arylstibinic chlorides retain more water than those isolated by the acidification of solutions of alkali arylstibinates. Phenylstibinic acid is represented by the formulæ $[3(C_6H_5SbO_2)H_2O].2H_2O$ and $[3C_6H_5SbO_2.H_2O].3H_2O$, since two or three molecules of water may be removed by drying in a vacuum over sulphuric acid, whereas the last molecule requires a high temperature for its removal. The action of the acid towards alkali also supports this formulation, since Schmidt observed that it will dissolve completely in one-third of a molecular equivalent of sodium hydroxide and that the resulting solution, although at first neutral to phenolphthalein, gives an acid reaction on standing and requires further addition of alkali for neutralisation ; this addition may be continued until one molecular equivalent of alkali has been added, when no further change takes place, this pointing to the operation being one of hydration of the antimony atoms, during which the complex molecule is dissociated into the phenyl derivative of orthoantimonic acid. The foregoing observations on hydration are also repeated with potassium

hydroxide, but less readily with lithium hydroxide.[1] The phenomenon is noted also in the case of pyroantimonic acid,[2] which, on neutralisation with sodium hydroxide, using phenolphthalein as indicator, becomes acid again on standing or boiling. This is due to the formation of acid sodium orthoantimonate ; when the pyro-acid is completely converted, no further change takes place. A number of hydrates is also known to exist in the case of antimonic oxide, the final product depending on conditions of previous drying and method of hydration.[3]

The arylstibinic acids also possess the properties of colloids, similar to the case of the tri- and tetra-hydrates of antimony pentoxide.[4] An alkaline solution of a stibinic acid, when titrated with a mineral acid, soon becomes turbid, and when sufficient acid has been added to neutralise the whole of the alkali present, the turbidity becomes more marked. According to Schmidt the turbid solutions possess the properties of hydrosols, and an excess of acid is required to precipitate the colloidal acids from the turbid solutions.

The formation of complexes takes place with all primary arylstibinic acids, the substituents in the ring exerting an effect on the nature of the final product.

Macallum [5] does not agree with Schmidt's conception of the formulæ for primary arylstibinic acids, but supports the simple formula, $C_6H_5.SbO(OH)_2$, his ideas being based upon molecular weight determinations, but until further work has been done it would be unwise to give a verdict on this view.

Phenylstibinic acid, $[3(C_6H_5SbO_2)H_2O].nH_2O$ or $[3(C_6H_5SbO_2)2H_2O].nH_2O$, may be prepared in several ways : (1) From antimony trioxide and benzene diazonium chloride in the presence of alkali. The crude product is purified by conversion into ammonium phenyl chloroantimonate (p. 219), which is then hydrolysed by water.[6] (2) From the double compound of antimony trichloride and benzene diazonium chloride by the action of alkali.[7] (3) 93 grams of aniline are dissolved in 1000 c.c. of water and 147 grams of sulphuric acid and diazotised by 71 grams of sodium nitrite. A solution from 140 grams of antimony trioxide in 764 grams of hydrochloric acid (density 1·123) is treated with 600 grams of sodium hydroxide in 3000 c.c. of water and rapidly cooled to 0° C., when a portion of the sodium antimonite separates out. To the solution the diazonium solution is then added with rapid stirring. Copper paste is added, and nitrogen is readily evolved. After several hours the excess of alkali is nearly neutralised by dilute sulphuric acid, the mixture filtered, and the phenylstibinic acid precipitated by adding hydrochloric acid. The crude acid (100 grams) is dissolved by heat in 250 grams of hydrochloric acid (density 1·123) and the hot solution saturated with solid ammonium chloride. Shining plates of phenylstibinic oxychloride separate and are washed with a saturated solution of ammonium chloride in hydrochloric acid. The crystals are then dissolved in a slight excess of

[1] Schmidt, *Annalen*, 1922, 55, 697.
[2] Delacroix, *J. de Pharm.*, 1897, [6], 6, 337.
[3] Senderens, *Bull. Soc. chim.*, 1899, [3], 21, 49; Delacroix, *ibid.*, 1899, [3], 21, 1049; 1901, [3], 25, 288.
[4] Jander, *Kolloid. Zeitsch.*, 1918, 23, 122.
[5] Macallum, *J. Soc. Chem. Ind.*, 1923, 42, 468 T.
[6] Schmidt, *Annalen*, 1920, 421, 188.
[7] American Patent, 1260707; see May, *Trans. Chem. Soc.*, 1912, 101, 1033.

dilute sodium carbonate solution, the solution filtered and the acid precipitated by acidifying the filtrate with dilute acid.[1] (4) 93 grams of aniline and 220 grams of antimony trichloride are dissolved in 850 grams of hydrochloric acid (density 1·123) and 1000 c.c. of water added. The solution is diazotised with 71 grams of sodium nitrite and a solution of 400 grams of sodium hydroxide in 10,000 c.c. of water slowly run in, the mixture being cooled and vigorously stirred during the operation. A brisk evolution of nitrogen soon takes place, and the product is isolated from the reaction mixture as in the preceding process.[2] (5) Phenyldichlorostibine, obtained by heating triphenylstibine and antimony trichloride together in xylene solution, is suspended in ether and chlorinated. The resulting oil is treated with ammonium hydroxide and the phenylstibinic acid precipitated from the filtrate by acidification with hydrochloric acid.[3]

Phenylstibinic acid is a white solid, not melting below 250° C., slightly soluble in alcohol, more soluble in acetone, and separating from hot acetic acid in fine crystals. It dissolves in warm chloroform or amyl acetate, and is readily soluble in cold alcohol-benzene, alcohol-ether or alcohol-chloroform mixture, separating from the last-named as diamond-shaped glistening crystals on the addition of a little water. It is soluble in dilute alkalis, yielding salts, and the *barium salt* is precipitated by adding barium chloride to an ammoniacal solution of the acid. The acid reacts with hydrogen sulphide to yield a pale yellow sulphide, decomposed on warming with partial formation of antimony sulphide.[4]

4-Chlorophenylstibinic acid,

A solution of 50 grams of *p*-chloroaniline in 250 grams of hydrochloric acid (density 1·123) and 150 grams of water is diazotised by the addition of a solution of 29 grams of sodium nitrite. To this solution are added 84 grams of antimony trichloride in 110 grams of hydrochloric acid (density 1·123) and 50 grams of water. The thick yellowish precipitate which separates is washed with dilute hydrochloric acid, suspended in 1500 grams of water and treated with 150 grams of sodium hydroxide (density 1·47). Nitrogen is slowly evolved, and when the evolution is complete the mass is filtered and the solid extracted many times with warm dilute sodium hydroxide solution. Acidification of the combined filtrates precipitates *p*-chlorophenylstibinic acid, which is filtered off, dried, dissolved in 110 grams of warm hydrochloric acid (density 1·123) and treated with a little animal charcoal. After filtration the solution is saturated with solid ammonium chloride, when 4-chlorophenylstibinic oxychloride is precipitated. This is washed with a saturated solution of ammonium chloride in hydrochloric acid (density 1·123) to remove inorganic antimony compounds. The residue is dissolved in dilute sodium hydroxide, and after filtration the stibinic acid is precipitated by dilute hydrochloric acid.[5]

[1] German Patent, 254421; English Patent, 16350 (1912).

[2] German Patent, 261285. [3] May, *loc. cit.*; Hasenbäumer, *Ber.*, 1898, 31, 2913.

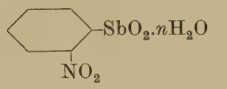
[4] For the preparation of neutral-reacting, alkali-soluble aromatic stibinic acids, see German Patent, 267083.

[5] German Patent, 261825; May, *Trans. Chem. Soc.*, 1912, 101, 1037; Schmidt, *Annalen*, 1920, 421, 207.

4-Chlorophenylstibinic acid is a colourless powder, soluble in mixtures of alcohol with benzene, chloroform or carbon disulphide, from which it separates in a crystalline condition. The compound decomposes without melting on heating.

4-Bromophenylstibinic acid, $BrC_6H_4.SbO(OH)_2$, occurs when diazotised *p*-bromoaniline is treated with antimony trioxide in the presence of alkali. The mixture is decolorised by animal charcoal and dilute sulphuric acid added until the solution is nearly neutral to litmus, any precipitate being filtered off. The solution is then made neutral to Congo red by the addition of dilute acid, when the stibinic acid is precipitated as a pale buff-coloured body.[1]

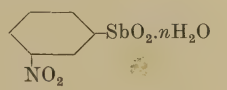
2-Nitrophenylstibinic acid,



A solution of 13·8 grams of *o*-nitroaniline in 100 c.c. of 5*N* nitric acid is diazotised in the usual manner, and after cooling with ice is treated with 40 c.c. of 5*N* sodium hydroxide solution and a solution of 33 grams of tartar emetic. The mixture is stirred and sodium hydroxide solution run in until a vigorous evolution of nitrogen takes place, this requiring about 40 c.c. of 5*N* sodium hydroxide. When a test portion no longer couples, the whole is made strongly alkaline, then acidified and warmed. The precipitated stibinic acid is filtered off and dried. To remove impurities the acid is treated with concentrated hydrochloric acid, then dissolved in alcoholic hydrochloric acid, from which solution impurities may be precipitated by carefully adding water. After filtration the stibinic acid is precipitated by the addition of water.[2]

o-Nitrophenylstibinic acid is a yellowish-brown powder, remaining unchanged at 285° C. It is sparingly soluble in methyl and ethyl alcohols, even after the addition of chloroform, but it dissolves in a large bulk of boiling acetic acid and in dilute alkali. Methyl alcohol-hydrochloric acid mixture converts it into the stibinic chloride.[3] When boiled with an excess of sodium hydrogen tartrate the acid forms a *tartrate*, $NO_2.C_6H_4.SbO(OH)_2.C_4H_5O_6Na$.

3-Nitrophenylstibinic acid,



This acid may be obtained in two ways : (1) *m*-Nitroaniline is diazotised and treated with tartar emetic in slightly acid solution, but the yield is very small.[4] (2) By adding phenylstibinic acid to well-cooled fuming nitric acid (density 1·51) and purifying by means of the chloride, as in the case of phenylstibinic acid. The acid also occurs when 12 parts of nitric acid (density 1·5) and 4 parts of concentrated

[1] Fargher and Gray, *J. Pharm. and Exper. Therap.*, 1921, 18, 354.

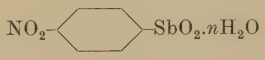
[2] Schmidt, *ibid.*, p. 205.

[3] Macallum (*J. Soc. Chem. Ind.*, 1923, 469 T) disagrees with Schmidt's formulation of this acid and states that molecular weight determinations of this acid and also of *p*-aminophenylstibinic acid in phenol solution give figures which point to these derivatives being monomolecular.

[4] Schmidt, *ibid.*, p. 202.

sulphuric acid are used as the nitrating mixture at 40° to 55° C.[1] It is a pale yellow powder, unmelted below 290° C., and has a similar solubility to the preceding acid. It is decomposed when heated with phosphorus pentabromide and chloroform at 100° to 110° C., giving 1-bromo-3-nitrobenzene in 70 per cent. yield.

4-Nitrophenylstibinic acid,



p-Nitroaniline is diazotised in the usual manner and treated with antimony trichloride. The double salt, $NO_2.C_6H_4.N_2Cl.SbCl_3$, is then decomposed by suspending it in water and adding a slight excess of sodium hydroxide. Addition of hydrochloric acid precipitates the stibinic acid, which is filtered off, dried, washed with hydrochloric acid, dissolved in alcoholic hydrochloric acid and reprecipitated by water. It is a chrome-yellow powder, decomposing at about 300° C.[2]

2-Aminophenylstibinic acid, $NH_2.C_6H_4.SbO_2.H_2O$, occurs when the corresponding nitro-compound is reduced by ferrous hydroxide or by titanous chloride in methyl alcohol solution.[3] The acid is a brownish powder, darkening above 150° C., and soluble in about 200 parts of water. It dissolves in methyl alcohol, warm glycerine, dilute acetic acid and sodium hydroxide, the alkali solution giving precipitates with most alkaline earth and heavy metals with the exception of zinc and magnesium. Aqueous solutions of the acid or its salts decompose on standing. The *lead salt* has the composition $C_{12}H_{12}O_6N_2Sb_2Pb.8H_2O$ and the *barium salt* $C_6H_6O_3NSbBa.4H_2O$. When the acid is treated in neutral solution with an excess of acetic anhydride at 0° C., it yields an *acetyl derivative*, which does not melt below 250° C., is sparingly soluble in water, and readily soluble in formic acid, dilute acetic acid or warm glycerine ; it yields the usual soluble alkali and ammonium salts.[4]

3-Aminophenylstibinic acid, $NH_2.C_6H_4.SbO_2.nH_2O$, may be prepared as follows : (1) *m*-Aminophenyldichlorostibine hydrochloride is suspended in a mixture of ice and water and treated with an excess of ammonium hydroxide and the calculated amount of hydrogen peroxide. From the resulting solution the stibinic acid is separated by the addition of acetic acid, excess of precipitant being avoided or the precipitate redissolves.[5] The stibinic acid is a white powder, darkening at high temperatures without melting. It is insoluble in methyl or ethyl alcohol, readily soluble in acids and alkalis. It can be diazotised and coupled in the usual manner, and with aromatic aldehydes forms coloured Schiff's bases. The acid gives rise to a *sulphide* and a *sulphate*, and it may be acetylated using the Schötten-Baumann reaction.[6]

[1] Morgan and Micklethwait, *J. Chem. Soc.*, 1911, 99, 2296; compare German Patent, 287709.

[2] Charrier, *Gazzetta*, 1922, 52, ii, 16.

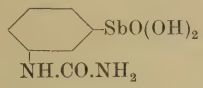
[3] Macallum, *loc. cit.*

[4] Breinl and Nierenstein (*Ann. Trop. Medicine and Parasit.*, 1908–1909, ii, 381) state that they prepared 2-aminophenylstibinic acid from *o*-chloroaniline and magnesium in dry ether solution by adding antimonic acid, but such a reaction appears impossible and their compound does not correspond with Macallum's derivative.

[5] Schmidt, *loc. cit.*, p. 226; see German Patent, 270488.

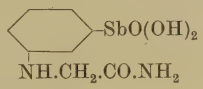
[6] German Patent, 284231.

m-Carbamidophenylstibinic acid,[1]



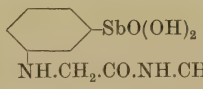
m-Aminophenylstibinic acid, 6 grams, in 20 c.c. of normal hydrochloric acid, is neutralised by sodium hydroxide and treated with 25 c.c. of acetic acid followed by a concentrated aqueous solution containing 2·5 grams of potassium cyanate at 0° C. After an hour the precipitate is collected, dissolved in sodium hydroxide and reprecipitated by hydrochloric acid. Purification is effected by suspending 5·5 grams of the crude product in 50 c.c. of concentrated hydrochloric acid at 0° C. and after three hours filtering off the yellow crystalline stibinic chloride, washing it with hydrochloric acid and hydrolysing it to the stibinic acid by water. The product is a white amorphous powder which decomposes without melting when heated. The *sodium salt* is a white amorphous powder, moderately soluble in water.

N-Phenylglycineamide-m-stibinic acid,



A solution of 5·2 grams of *m*-aminophenylstibinic acid and 3·6 grams of chloracetamide in 20 c.c. of normal sodium hydroxide is heated at 90° C. for 90 minutes. Sufficient sodium hydroxide is then added to dissolve the precipitate which forms and the solution treated with a further 1·5 grams of chloracetamide and heated for another 60 minutes to complete the condensation. The clear solution obtained by adding the requisite amount of alkali is acidified with acetic acid, the precipitated stibinic acid dissolved in 15 c.c. of 2*N* hydrochloric acid, the addition of ice-cold hydrochloric acid (15 c.c., density 1·19) then resulting in the separation of the crystalline *stibinic chloride*. This is quickly filtered off, dissolved in water, the solution made alkaline and the free stibinic acid reprecipitated by the addition of acetic acid. The acid is a white amorphous powder, readily soluble in dilute alkali or excess of dilute mineral acid, but insoluble in dilute acetic acid. Sodium nitrite precipitates a gelatinous *nitrosamine* when added to a dilute hydrochloric acid solution of the stibinic acid. The *sodium salt* is a white amorphous powder, readily soluble in water.

N-Phenylglycinemethylamide-m-stibinic acid,



is obtained by a similar method to the foregoing compound. It gives a strong odour of methylamine when heated with sodium hydroxide solution. The *sodium salt* is a white amorphous powder, completely soluble in about half its weight of water. The condensation has also been effected using chloroacetethylamide.

4-Aminophenylstibinic acid, $NH_2.C_6H_4.SbO_2.nH_2O$.—4-Acetylaminophenylstibinic acid, 50 parts, is heated for several hours on the

[1] Morgan and Cook, *J. Chem. Soc.*, 1930, p. 737.

water-bath with 500 parts of 5 per cent. sodium hydroxide solution, until a test portion when largely diluted gives a precipitate with dilute hydrochloric acid which immediately dissolves in excess of the reagent. The free acid is then precipitated from the solution by the addition of dilute acetic acid.[1] Saponification of the acetyl derivative may also be effected by warming with 5*N* potassium hydroxide solution at 90° C. for one hour.[2] The crude acid may be purified by treatment with ice-cold hydrochloric acid (density 1·19), when the *chloride*, $(NH_2.HCl)C_6H_4.SbCl_4$, is produced, this subsequently being decomposed by the calculated quantity of sodium hydroxide.

A more recent method of preparation is as follows:[3] A mixture of the calculated amounts of *p*-aminoacetanilide and antimony trioxide in sufficient 15 per cent. hydrochloric acid to dissolve the trioxide is diazotised with 15 per cent. sodium nitrite solution. The latter is introduced through a capillary tube reaching to the bottom of the beaker, the contents of the latter being mechanically stirred. A yellow crystalline molecular compound is formed, filtered off, suspended in water, cooled to 3°–5° C., and 10 per cent. sodium hydroxide added in small portions, efficient stirring being maintained. If great care is not exercised a stiff foam forms and the yield is low. When the vigorous evolution of nitrogen ceases, the solution is nearly neutralised, carbon dioxide passed in and the resulting precipitate filtered off and discarded. The filtrate is then acidified with dilute acetic acid, a yellowish-white flocculent precipitate separating. This is best removed by centrifuging. It is claimed that by this process and subsequent hydrolysis a 35 to 60 per cent. yield of *p*-aminophenylstibinic acid results.[4]

4-Aminophenylstibinic acid is a colourless powder, insoluble in the usual organic solvents, readily soluble in dilute sodium hydroxide, from which alcohol precipitates the *sodium salt*. The acid decomposes on heating, without melting, but the sodium salt is more stable than the free acid. When the salt is warmed with potassium iodide and dilute sulphuric acid, *p*-iodoaniline is formed. The acid condenses with aldehydes in the presence of an excess of acetic acid, and diazotisation and coupling with β-naphthol in alkaline solution gives a red azo-derivative.[5] *The sodium salt is the antimony analogue of* "*atoxyl.*" When urea is added to a warm aqueous solution of the acid and the mixture is concentrated, the subsequent addition of alcohol precipitates a compound to which the following structure has been assigned:[6]

The following amine salts of *p*-aminophenylstibinic acid are also known: *dimethylamine* and *trimethylamine salts*, *ethylamine*, *diethylamine* and *triethylamine salts*, *propylamine salt*, *isoamylamine salt* and *allylamine salt*. All these salts are soluble in water giving red solutions which cloud in a few minutes; they are insoluble in all organic solvents

[1] German Patent, 270488.
[2] Schmidt, *Annalen*, 1922, 429, 145.
[3] Dunning and Reid, *J. Amer. Chem. Soc.*, 1926, 48, 2959.
[4] Compare American Patent, 1682269.
[5] German Patent, 254421.
[6] Brahmachari, *Indian J. Med. Research*, 1922, 10, 508; Brahmachari and Das, *ibid.*, 1924, 12, 423; compare Niyogi, *J. Indian Chem. Soc.*, 1928, 5, 753; compare Balaban, *J. Chem. Soc.*, 1930, p. 1685.

except glycerine. Three molecules of the acid are combined with one molecule of the base.[1]

4 - Acetylaminophenylstibinic acid, $CH_3.CO.NH.C_6H_4.SbO_2.nH_2O$.—Monoacetyl-*p*-phenylenediamine, 150 grams, in 147 grams of sulphuric acid and 1000 grams of water, is cooled and diazotised by adding a solution of 71 grams of sodium nitrite. The diazotised solution is added to the calculated amount of sodium antimonite, and when the reaction is complete the solution is nearly neutralised by dilute sulphuric acid and saturated with carbon dioxide to remove impurities and excess alkali. After filtering, sodium chloride is added, when the *sodium salt* of the acid separates. This is freed from sodium chloride by dissolving in methyl alcohol and evaporating the solution. The sodium salt readily dissolves in water, forming a neutral solution from which mineral acids precipitate the free acid.[2] The acid is soluble in ammonium hydroxide, and alkali hydroxides or carbonates. The acetyl group may be removed as already indicated.[3]

The following derivatives have been obtained by applying the Bart-Schmidt reaction to the appropriate amino-compounds: *sodium benzyl-benzoate-4-stibinate*, *-3-stibinate*, *-2-stibinate* and *-5′-stibinate*.[4]

Carbethoxy-p-aminophenylstibinic acid, $C_2H_5OCO.NH.C_6H_4.SbO_2.H_2O$.—The aminostibinic acid in alkaline solution is condensed with ethyl chlorocarbonate and the product precipitated by acidification with hydrochloric acid.[5]

Replacement of the ethyl chlorocarbonate in the foregoing by benzene sulphonyl chloride and carrying out the reaction at 60° C. yields *benzenesulphonyl-p-aminophenylstibinic acid*, $C_6H_5.SO_2.NH.C_6H_4.SbO_2.H_2O$.[6]

When an alkaline solution of the *p*-aminophenylstibinic acid is refluxed for two hours with chloracetamide, *N-phenylglycineamide-p-stibinic acid* results, $NH_2.CO.CH_2.NH.C_6H_4.SbO_2.H_2O$. The product is purified by solution in sodium hydroxide and acidification with dilute acetic acid. The *sodium salt* of this acid is analogous to "*tryparsamide*."

Sodium *p*-aminophenylstibinate and allyl thiocarbamide condense in methyl alcohol solution at room temperature in 24 hours. Dilution of the solution and acidification yield *allylthiocarbamino-p-aminophenylstibinic acid*, $C_3H_5NH.CS.NH.C_6H_4.SbO_2.H_2O$, a pale yellow amorphous powder, soluble in sodium hydroxide but not in sodium carbonate.

Salicyl aldehyde and sodium *p*-aminophenylstibinate in acetic acid solution condense to yield *o-oxybenzylidene-p-aminophenylstibinic acid*.[7]

The following are obtained from *p*-aminophenylstibinic acid and the appropriate alkyl chloroformate in normal sodium carbonate solution :[8] *Carbomethoxy-*, *carbopropoxy-*, *carboisopropoxy-*, *carbobutoxy-*, *carbo-isobutoxy-*, *carbo-β-chloroethoxy-* and *carbo-γ-chloropropoxy- p-amino-phenylstibinic acids*. The last two are converted by 5 per cent. sodium hydroxide at 70° C. into *p-β-hydroxyethylaminophenylstibinic acid* and *p-γ-hydroxypropylaminophenylstibinic acid*, respectively.

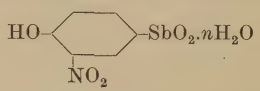
[1] Niyogi, *J. Indian Chem. Soc.*, 1928, 5, 285.
[2] German Patent, 254421; American Patent, 1260707; English Patent, 16350 (1912).
[3] For complex compounds derived from this acid, see German Patent, 396864.
[4] Niyogi, *J. Indian Chem. Soc.*, 1930, 7, 577.
[5] Brahmachari, *loc. cit.*
[6] Compare German Patent, 284231.
[7] German Patent, 284231.
[8] Hamilton and Etzelmiller, *J. Amer. Chem. Soc.*, 1928, 50, 3360.

Sodium p-ω-sulphomethylaminophenylstibinate, $(SO_3Na.CH_2.NH.C_6H_4.SbO_2)_3H(ONa)$,[1] is formed by treating sodium *p*-aminophenylstibinate in aqueous solution with formaldehyde and sodium hydrogen sulphite. Using " urea stibamine " in the preparation yields the *carbamide salt* of *p-ω-sulphomethylaminophenylstibinic acid, i.e.* $(SO_3Na.CH_2.NH.C_6H_4.SbO_2)_3H(OCH_3N_2O)$. When carbamide is allowed to react with the appropriate stibinic acid in aqueous solution, *carbamide p-acetamidophenylstibinate* and *carbamide p-hydroxyphenylstibinate* are isolated.

4-Hydroxyphenylstibinic acid, $HO.C_6H_4.SbO_2.nH_2O$, is obtained as follows: (1) Antimony trioxide in hydrochloric acid solution is allowed to react with diazotised *p*-aminophenol and the mixture then treated with 5*N* sodium hydroxide. After the product has been precipitated by acidification, it is dissolved in cold concentrated hydrochloric acid and a solution of pyridine in hydrochloric acid added. The *pyridine double salt* of the stibinic chloride is thus precipitated as an air-stable yellow substance, M.pt. 176° C. This salt is decomposed by cold water, the resulting stibinic acid taken up in sodium hydroxide and precipitated by acid.[2] (2) *p*-Aminophenol, 109 grams, is dissolved in 147 grams of sulphuric acid and 1000 grams of water and diazotised by adding a solution containing 71 grams of sodium nitrite. This diazo-solution is added to a sodium antimonite solution prepared as described under phenylstibinic acid. After completion of the reaction the mixture is saturated with carbon dioxide and filtered. The filtrate is saturated with sodium chloride and the 4-hydroxyphenylstibinic acid precipitated by the addition of dilute sulphuric acid.[3]

The acid is a colourless powder darkening when heated, but remaining unmelted at 270° C. It is fairly soluble in methyl alcohol or boiling water, sparingly soluble in cold water, the aqueous solution giving a violet coloration with ferric chloride. Addition of ammonium chloride to an ammoniacal solution of the acid causes precipitation of the *ammonium salt.* Solutions of the acid in hydrochloric acid (density 1·17) after standing give a test for inorganic antimony when hydrogen sulphide is passed through the solution. When an alkaline solution of the acid is treated at 60° C. with chloracetic acid, acidification with hydrochloric acid after three hours yields *carboxymethyleneoxyphenyl-4-stibinic acid,* $HO_2C.CH_2.O.C_6H_4.SbO_2.H_2O$.[4]

3-Nitro-4-hydroxyphenylstibinic acid,



may be obtained by two methods: (1) The 3-nitro-4-chlorophenylstibinic acid resulting from the nitration of 56 grams of *p*-chlorophenylstibinic acid is dissolved in sodium hydroxide solution, reprecipitated by hydrochloric acid and filtered off. The precipitate is washed and transferred whilst moist to a vessel containing 75 c.c. of potassium hydroxide (1 : 1) and the mixture heated for several hours at 90° C. The *potassium salt* is deposited, the liquor being cooled and treated

[1] Brahmachari and Gupta, *J. Asiatic Soc. Bengal,* 1929, 25, 301.
[2] Schmidt, *Annalen,* 1922, 429, 147.
[3] German Patent, 254421.
[4] Brahmachari, *loc. cit.*

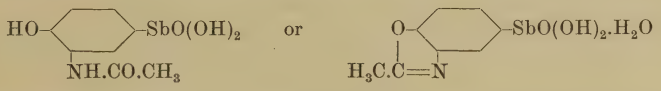
with alcohol. The salt is purified by solution in water and precipitation by alcohol, after which its aqueous solution is treated with mineral acid to liberate the free acid. An air-dried specimen obtained by this method corresponded to the formula $[3(NO_2.OH.C_6H_4.SbO_2).2H_2O].5H_2O$.[1] (2) 3-Nitro-4-acetylaminophenylstibinic acid, 35 grams, is heated with 300 grams of aqueous potassium hydroxide (density 1·30) until ammonia ceases to be evolved. Dilute sulphuric acid is then added to precipitate the stibinic acid.[2]

3-Nitro-4-hydroxyphenylstibinic acid is a brownish-yellow powder which does not melt below 230° C. Its solution in methyl alcohol gives no precipitate when water is added. It dissolves readily in acetic acid, aqueous alkalis and ammonium hydroxide. Warm concentrated hydrochloric acid dissolves it and on cooling *3-nitro-4-chlorophenylstibine tetrachloride* separates, the addition of ammonium chloride causing the deposition of the stable double salt. The *potassium salt* is a scarlet, crystalline powder.

3-Amino-4-hydroxyphenylstibinic acid, $(NH_2)(HO)C_6H_3.SbO_2.nH_2O$.—This acid is isolated by reducing the corresponding nitro-compound :[3] (1) 3-Nitro-4-hydroxyphenylstibinic acid, 30·8 grams, in 160 grams of water and 4 grams of sodium hydroxide, is reduced by adding 65 grams of sodium hydrosulphite in 200 c.c. of water containing 2 grams of sodium hydroxide. The mixture is well cooled, and as the red colour disappears the amino-acid separates as a white precipitate. The excess of hydrosulphite is removed by passing a current of air through the mixture. (2) The amino-acid may also be obtained by reducing the nitro-acid in aqueous solution by means of sodium amalgam.

The acid is an unstable white powder which soon darkens even in the dry state. When heated it decomposes without melting, and in water and the usual solvents it is insoluble, but it dissolves readily in alkali, ammonium hydroxide and acids. A *sodium salt* may be precipitated from the aqueous alkali solution by the addition of alcohol. The amino-group is diazotisable and the diazo-compound couples with alkaline resorcinol solution and other phenols.

3-Acetamido-4-hydroxyphenylstibinic acid,[4]

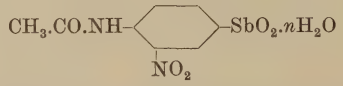


The foregoing amino-acid, obtained by the reduction of 16 grams of potassium 3-nitro-4-hydroxyphenylstibinate, is suspended in 12 c.c. of water and acetylated by the gradual addition of 9 c.c. of acetic anhydride. A clear solution results and after twenty-four hours several volumes of acetone are added, causing the precipitation of a stibinic acid which may be represented by one of the above formulæ. The substance is a white amorphous powder, extremely soluble in water, with an acid reaction, insoluble in acetone, alcohol or glacial acetic acid, and yielding a *sodium salt* which is readily soluble in water.

[1] Schmidt, *Annalen*, 1920, **421**, 212; German Patent, 262236.
[2] German Patent, 259875.
[3] German Patent, 270488.
[4] Morgan and Cook, *J. Chem. Soc.*, 1930, p. 743.

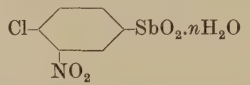
A more recent investigation [1] attacks the problem of the preparation of this acid in a different way : 8·25 grams of 4-amino-2-acetamidophenol and 11·4 grams of antimony trichloride in 7·5 c.c. of hydrochloric acid are added to 45 c.c. of water and 7·5 c.c. of hydrochloric acid, and the mixture treated at 0° C. with 3·45 grams of sodium nitrite in 23 c.c. of water; after three hours the antimony double salt of the diazo-compound is collected and added in small quantities to 150 c.c. of ice-cold 2*N* sodium hydroxide. The mixture is stirred for four hours, kept overnight, and filtered and acidified to Congo-red with hydrochloric acid, when about 8·1 grams of the crude stibinic acid are precipitated. This is dissolved in 2*N* ammonium hydroxide, an excess of hydrochloric acid added, the solution treated with charcoal, filtered, neutralised to Congo-paper with sodium acetate, and poured into a large volume of water. The acid separates as a white powder, becoming light brown when dried *in vacuo*. The yield is 1·8 grams. A specimen sealed in an ampoule for $3\frac{1}{2}$ years was readily soluble in 2*N* ammonium hydroxide, whereas one kept in an ordinary specimen tube was not wholly soluble after a similar lapse of time.

3-Nitro-4-acetylaminophenylstibinic acid,



Anhydrous sodium 4-acetylaminophenylstibinate, 113 grams, prepared by prolonged heating of the hydrated salt at 110° C., is dissolved in 300 grams of glacial acetic acid and the solution cooled to −10° to −2° C. To this solution 800 grams of concentrated sulphuric acid are added, followed by a mixture of 25·4 grams of nitric acid (density 1·515) and 100 grams of concentrated sulphuric acid, the temperature being maintained below 0° C. during the operation and the whole efficiently stirred. The stirring is continued for several hours and the reaction mixture then poured into ice-water. The crude nitro-acid separates and is removed, washed with water and dried. It is a yellowish-brown powder, readily soluble in alkalis, alkali carbonates and ammonium hydroxide, from which solutions it may be reprecipitated by acids. When heated it decomposes without melting.[2]

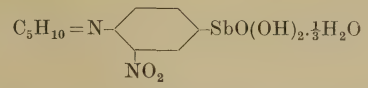
3-Nitro-4-chlorophenylstibinic acid,



28 grams of 4-chlorophenylstibinic acid are dissolved in 200 c.c. of concentrated sulphuric acid, keeping the temperature below 25° C. The temperature is then maintained below 5° C. whilst a mixture of 4·2 c.c. of nitric acid (density 1·515) and 5 c.c. of concentrated sulphuric acid is added. After a further hour's stirring the mixture is poured upon ice, when the nitro-acid separates. It is a colourless powder, unchanged at 250° C., readily soluble in warm methyl and ethyl alcohols, dilute alkalis or hydrochloric acid. Water does not reprecipitate the acid from alcoholic solution.[3]

[1] Balaban, *J. Chem. Soc.*, 1930, p. 1685.
[2] German Patents, 259875, 287709.
[3] Schmidt, *Annalen*, 1920, **421**, 208; compare German Patent, 262236.

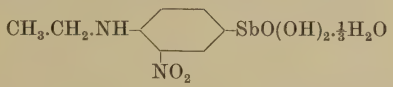
3-Nitro-4-piperidinophenylstibinic acid,[1]



A solution of 3·28 grams of 4-chloro-3-nitrophenylstibinic acid and 5·5 c.c. of piperidine in 20 c.c. of alcohol is boiled for three hours and then poured into water. The orange precipitate, 3·5 grams, is dissolved in 20 c.c. of warm glacial acetic acid and the cooled solution treated with 20 c.c. of concentrated hydrochloric acid, the *stibinic chloride hydrochloride* being precipitated. This is a colourless microcrystalline powder, decomposing at 185° to 187° C. When suspended for several hours in a large volume of water, 3-nitro-4-piperidinophenylstibinic acid hydrochloride separates as an orange amorphous powder. The latter is dissolved in alcohol by the aid of 2*N* sodium hydroxide and the clear solution acidified with acetic acid. The gelatinous precipitate which forms is dried and washed with water to remove occluded salts, being obtained as an orange amorphous powder, sparingly soluble in excess of dilute aqueous alkali.

3-Amino-4-piperidinophenylstibinic acid, $C_5H_{10}=N.C_6H_3(NH_2)SbO(OH)_2.\frac{1}{3}H_2O$, occurs when the foregoing nitro-acid is reduced with ferrous hydroxide. It is a greyish powder, soluble in very dilute mineral acid or alkali, the solutions giving the reactions for primary amines. The *sodium salt* has been isolated.

3-Nitro-4-ethylaminophenylstibinic acid,



is the condensation product of 4-chloro-3-nitrophenylstibinic acid and ethylamine in alcohol solution, the reaction being completed in three hours at 120° to 130° C. The crude product is converted to the *stibinic chloride*, a buff, microcrystalline powder, having no definite melting-point. Hydrolysis of this chloride by water yields the orange stibinic acid, which may be further purified through its ammonium salt.

3-Nitro-4-methylaminophenylstibinic chloride is prepared in the same manner as the ethylamino-compound.

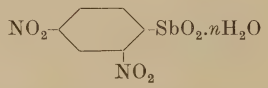
3 : 5-Dichloro-4-acetamidophenylstibinic acid.[2]—4-Acetamido-3 : 5-dichloroaniline (2·5 grams) in 20 c.c. of water and 10 c.c. of hydrochloric acid is diazotised at 0° C. and a further 10 c.c. of hydrochloric acid added. To the solution are added 2 grams of antimony trioxide in 20 c.c. of hydrochloric acid. A yellowish-white precipitate separates and is left in ice for 30 minutes with occasional stirring. It is filtered off, washed with dilute hydrochloric acid and then with water until acid-free. The moist mass is then triturated with water, cooled to 5°–7° C. and 6 grams of sodium hydroxide in water gradually added with vigorous stirring, the stirring being continued until evolution of nitrogen slackens. The liquid is then filtered and the clear filtrate acidified with dilute acetic acid, when the free antimonic acid separates as a flocculent precipitate. This is washed with water until free from admixed acid, suspended in water and brought into solution by adding

[1] Morgan and Cook, *J. Chem. Soc.*, 1930, p. 737.
[2] Niyogi, *J. Indian Chem. Soc.*, 1927, 4, 397.

dilute sodium carbonate solution dropwise. The solution is evaporated to dryness in a vacuum, the residue extracted with methyl alcohol, boiled with charcoal and filtered, the *sodium salt* of the antimonic acid being precipitated from solution by the addition of ether. The dry product is a pale red amorphous powder, moderately soluble in water, giving a red solution which is neutral to litmus. The free acid may be precipitated by acidification with dilute mineral acid.

The following *sodium salts* are isolated by the same method and have similar properties to those just given : *3 : 5-dibromo-* and *3 : 5-di-iodo-4-acetamidophenylstibinates*, *3-bromo-* and *3-iodo-4-acetamidophenyl-stibinates*.

2 : 4-Dinitrophenylstibinic acid,



occurs when 2 : 4-dinitroaniline is diazotised and treated with tartar emetic in neutral or slightly acid solution in the usual manner. It is a brown powder, exploding when heated.[1]

p-Tolylstibinic acid, $CH_3.C_6H_4.SbO(OH)_2$.—Two solutions, one of diazotised *p*-toluidine (26 grams of base, 37 grams of concentrated sulphuric acid, 250 c.c. of water and 18 grams of sodium nitrite) and the other of 56·6 grams of antimony trichloride in 15 grams of hydrochloric acid (density 1·16) and 41 c.c. of water to which 150 grams of sodium hydroxide in 750 c.c. of water have been added, are mixed at 0° C. and treated with copper bronze. The liquid is filtered after two days, nearly neutralised with dilute sulphuric acid, again filtered if necessary, and acidified with dilute hydrochloric acid. The mixture (50 grams) of *p*-tolylstibinic acid and antimony trioxide thus obtained is dissolved in 27 grams of hydrochloric acid (density 1·16) and 98 c.c. of water and the boiling solution saturated with solid ammonium chloride. The mixture of *p-tolylstibinic oxychloride* and ammonium chloride that crystallises on cooling is filtered off and dissolved in sodium carbonate solution, the stibinic acid is precipitated by acidification with dilute hydrochloric acid, and crystallised from spirit and from ether.[2] Yield, 8 grams. The acid also occurs when *p*-tolylstibinic tetrachloride is hydrolysed.[3] The product from both methods is a white amorphous powder.

p-Anisylstibinic acid, $CH_3O.C_6H_4.SbO_2.nH_2O$.—This acid is obtained from *p*-anisidine by the method used for phenylstibinic acid from aniline.[4] It has not been analysed. It interacts with an excess of hydrochloric acid, yielding a yellow, crystalline, deliquescent *chloride*, which is easily decomposed with elimination of antimony. The acid itself is less stable than most stibinic acids.

p-Phenetylstibinic acid, $C_2H_5O.C_6H_4.SbO_2.nH_2O$, occurs when *p*-phenetidine is diazotised and treated with antimony trioxide in the usual manner. By stirring the crude acid with hydrochloric acid containing ammonium chloride, the *double salt* of the *stibinic chloride* with *ammonium chloride* results. This is dissolved in cold methyl alcohol,

[1] German Patent, 296940.
[2] Goddard and Yarsley, *J. Chem. Soc.*, 1928, p. 721.
[3] Hasenbäumer, *Ber.*, 1898, **31**, 2914.
[4] Schmidt, *Annalen*, 1920, **421**, 213.

the solution treated with animal charcoal, filtered, and the acid precipitated by diluting the filtrate with water. Final purification is effected by solution in alkali and reprecipitation by acid.[1] The acid is a colourless powder, having an odour resembling that of phenetole. It darkens on being heated, but remains unmelted at 270° C. In mixtures of chloroform with alcohols, alcohol-benzene or acetic acid, it is readily soluble, but is not completely soluble in methyl alcohol or chloroform by itself. Hydrochloric acid converts the acid into a stibinic chloride which is unstable and resembles the foregoing anisyl compound.

Mono-biphenylstibinic acid,[2] $C_6H_5.C_6H_4.SbO(OH)_2$, obtained by treating the tetrachloride with water, is a white powder, decomposing above 300° C. The tetrachloride required for this preparation is formed by the action of chlorine on a chloroform solution of the dichloride.

The following stibinic acids [3] are obtained from the corresponding amines by the method of Dunning and Reid,[4] described under 4-aminophenylstibinic acid, p. 230 : *p-carboxymethylphenyl-*, *p-carbethoxyphenyl-*, *p-carbethoxyaminophenyl-*, *acetophenone-4-*, *α-naphthyl-*, *4-aminodiphenyl-4′-*, *4-carbethoxyaminodiphenyl-4′-*, *4-aminodiphenylmethane-4′-*, *2-nitro-4-methoxyphenyl-*, *2-acetamido-5-methoxyphenyl-*, *2-acetamido-4-methoxyphenyl-*, *1 : 4-phenylenedi-*, and *4 : 4′-diphenylmethanedi- stibinic acids*. These products form buff powders, with the exception of acetophenone-4-stibinic acid, which is deep red.

When mixed aliphatic-aromatic antimony compounds containing carbonyl groups at non-cyclic bonds are treated with hydrazine or its derivatives, especially semicarbazide, or with other reactive amino-compounds, hydrazone products result.[5] Thus, an aqueous solution of *p*-acetophenonestibinic acid containing sodium hydroxide, on adding to semicarbazide hydrochloride, warming on a water-bath, filtering, and acidifying the clear filtrate with hydrochloric acid, precipitates the colourless hydrazone product, which is purified by solution in sodium carbonate and reprecipitation with acid. The substance thus isolated melts at 350° C. An alcoholic solution of 1-hydroxy-2-acetophenone-4-stibinic acid may be treated in a similar manner.

It is stated [6] that arylstibinic acids such as the phenyl-, *p*-chlorophenyl- and *m*-chloro-*p*-acetamidophenyl- acids, obtained by treating the appropriate diazotised amino-compound with antimony oxide, may be isolated in greatly improved yields by the presence of glycerol or other polyhydric alcohols. These substances inhibit the formation of by-products and the required acid is more readily isolated. Water-soluble derivatives of amino- or aminohydroxy- arylstibinic acids or their oxides may be formed by treating such derivatives with aldoses or ketoses;[7] the condensation is effected by heating the components in aqueous solution at 50° to 55° C. with the addition, if necessary, of a little sodium hydroxide. Examples given are the condensation of galactose with *m*-aminophenylstibinic acid and of lactose with *m*-aminophenylstibinous oxide.

[1] Schmidt, *Annalen*, 1922, 429, 148; Fargher and Gray, *J. Pharm. and Exper. Therap.*, 1921, 18, 354. [2] Worrall, *J. Amer. Chem. Soc.*, 1930, 52, 2046.
[3] Riddell and Basterfield, *Trans. Roy. Soc. Canada*, 1929, [iii], 23, III, 45.
[4] Dunning and Reid, *J. Amer. Chem. Soc.*, 1926, 48, 2959.
[5] German Patent, 469327. [6] English Patent, 244746 (1925). [7] German Patent, 433105.

Secondary Aryl stibinic Acids.

These acids are obtained by the following general methods :—

(1) Diarylstibinic chlorides are subjected to hydrolysis :

$$R_2SbCl \longrightarrow R_2SbCl_3 \longrightarrow R_2SbO(OH)$$

(2) Triarylstibines are subjected to oxidation, using hydrogen peroxide in the presence of alkali, which causes "dearylation" of the tertiary stibine :

$$R_3Sb \xrightarrow[H_2O_2]{NaOH} R_2SbO(ONa) + RH$$

(3) By the diazo reaction, the antimony oxide used in the preparation of the primary acids now being replaced by an arylstibinoxide : [1]

$$RN:NX + Sb\begin{matrix}R\\ \\ O\end{matrix} + 2KOH \longrightarrow RN:N.O.Sb\begin{matrix}R\\ \\ OK\end{matrix} + KX + H_2O$$

$$RN:N.O.Sb\begin{matrix}R\\ \\ OK\end{matrix} \longrightarrow RSb\begin{matrix}R\\ OK\\ O\end{matrix} + N_2$$

Obviously the foregoing scheme may be used for preparing symmetrical or unsymmetrical stibinic acids according as whether the aryl radical of the diazo-compound is the same or different from the aryl group of the arylstibinoxide.

All the diarylstibinic acids are solids, and their method of preparation has an influence upon their solubility, *e.g.* the hydrolysis of diphenylstibinic chloride by ammonium hydroxide yields an acid which is insoluble in ammonium hydroxide or sodium carbonate, but dissolves in sodium hydroxide, whilst solution of the chloride in sodium hydroxide gives a stibinic acid on acidification with acetic acid which dissolves in all the foregoing alkalis. The secondary acids also differ from the primary acids in their action towards hydrochloric acid and ammonium chloride ; diphenylstibinic acid is insoluble in concentrated hydrochloric acid, and in hot dilute hydrochloric acid its solutions do not give a double salt with ammonium chloride, but pyridine hydrochloride precipitates diphenylstibinic chloride as a double salt. Nitration of the secondary stibinic acids yields nitro-acids containing the nitro-group in the *meta*-position to the antimony. Reduction of the secondary acids yields stibinoxides. Mercuric chloride converts diphenylstibinic acid in methyl alcohol-hydrogen chloride solution into phenylmercuric chloride and antimony trichloride.

Diphenylstibinic acid, $(C_6H_5)_2SbO.OH$, may be isolated in several ways : (1) Aniline, 9·3 grams, in 60 c.c. of 5*N* hydrochloric acid, is diazotised, ice added, and a solution of 21 grams of phenylstibinous oxide in a small bulk of acetic acid run in. The solution is then made alkaline, when nitrogen is evolved. When the action has ceased the whole is filtered and acidified, the stibinic acid separating out. The acid is purified by solution in alkali and reprecipitation by sulphuric acid. If further purification is necessary the acid is dissolved in hot dilute hydrochloric acid, when the *chloride* is formed, $(C_6H_5)_2SbCl_3.H_2O$.

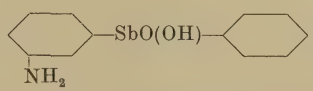
[1] Compare the corresponding arsenical compounds, this Volume, Part II, p. 154.

This is dissolved in spirit by the aid of a little hydrochloric acid and the solution poured into dilute sodium hydroxide, addition of acetic acid then causing separation of the stibinic acid as a voluminous precipitate.[1] (2) 8 grams of triphenylstibine in acetone solution are added slowly to a hot mixture consisting of 150 c.c. of water, 50 c.c. of 5*N* sodium hydroxide and 60 c.c. of 3 per cent. hydrogen peroxide, the mixture being stirred during the operation. After filtering, the diphenylstibinic acid is precipitated by dilute sulphuric acid and purified as follows: After collecting the product it is boiled whilst moist with 5*N* hydrochloric acid and precipitated as the *pyridine double salt* by adding pyridine hydrochloride (25 c.c. of pyridine in 100 c.c. of hydrochloric acid, density 1·19). This salt is dissolved in boiling 5*N* hydrochloric acid and, on cooling, crystals of diphenylstibine trichloride, $(C_6H_5)_2SbCl_3.H_2O$, M.pt. 175° C., are obtained. This is recrystallised from benzene and converted into the acid as already described. (3) Diphenylchlorostibine is converted into the stibinic chloride, which is then hydrolysed by alkali.[2]

Diphenylstibinic acid is a light powder, M.pt. 285° C. From acetic acid it crystallises in shining crystals, insoluble in concentrated hydrochloric acid, soluble in hot dilute hydrochloric acid. Its behaviour towards alkalis depends upon its method of preparation. If obtained by method (1), it is insoluble in dilute alkali. Alcoholic solutions of the trichloride yield with dilute ammonium hydroxide a granular precipitate of diphenylstibinic acid insoluble in sodium carbonate or ammonium hydroxide. The stibinic acid which separates when an aqueous sodium hydroxide solution of the trichloride is treated with acetic acid is readily soluble in both the foregoing solvents. Moreover, the product obtained by chloride hydrolysis in the form of an alkaline solution, if made just slightly alkaline to phenolphthalein by addition of sulphuric acid, gradually regains its alkalinity on standing. By repeating this process many times a diphenylstibinic acid results which is soluble in sodium hydroxide or carbonate, and ammonium hydroxide.

2 : 2′-Dichlorodiphenylstibinic acid, $(Cl.C_6H_4)_2SbO.OH$, occurs when *o*-chlorobenzene diazonium chloride is treated with antimony trioxide.[3] It is purified by conversion to the *chloride*, M.pt. 105° to 110° C., the latter being dissolved in alcohol, dilution of the solution with water yielding the acid. The product is sparingly soluble in alkalis; with potassium iodide and dilute sulphuric acid it gives an oil, which is probably *o*-iodochlorobenzene.

3-Aminodiphenylstibinic acid,



Aniline, 9·3 parts, in 650 parts of hydrochloric acid (density 1·085) and 400 parts of water, is diazotised with 71 parts of sodium nitrite. The diazo-solution is then mixed with an ice-cold solution prepared by dissolving 320 parts of 3-aminophenyldichlorostibine hydrochloride in 1500 parts of water containing 280 parts of sodium hydroxide. A vigorous evolution of nitrogen occurs, and when the reaction is complete

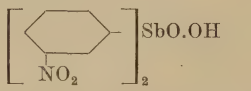
[1] Schmidt, *Annalen*, 1922, 429, 141, 236; German Patent, 394795.

[2] Michaelis and Reese, *Annalen*, 1886, 233, 59; Michaelis and Günther, *Ber.*, 1911, 44, 2319; Morgan and Micklethwait, *Trans. Chem. Soc.*, 1911, 99, 2296.

[3] Macallum, *J. Soc. Chem. Ind.*, 1923, 42, 469 T.

the stibinic acid is precipitated by adding acetic acid. The crude product is purified by converting it to the *hydrochloride* by means of concentrated hydrochloric acid. The hydrochloride, which gradually darkens above 200° C., is washed with 5*N* hydrochloric acid and dried. The product is now treated with ether until its colour no longer changes, then dissolved in dilute sodium hydroxide. The solution is faintly acidified, filtered, and treated with sodium acetate to precipitate the stibinic acid.[1] The acid is a powder which soon becomes pale red ; it sinters when heated to about 200° C., dissolves in dilute alkali, methyl and ethyl alcohols or chloroform, but is insoluble in ether or benzene.

3 : 3′-Dinitrodiphenylstibinic acid,



When diphenylstibinic chloride in alcoholic solution is treated with silver nitrate it yields diphenylstibinic basic nitrate. The latter is added to nitric acid (density 1·5) mixed with four volumes of concentrated sulphuric acid, and the temperature maintained at 40° C. and finally at 55° C. The crude stibinic acid is precipitated by mixing the reaction product with ice-water. The resulting substance is collected, dissolved in normal sodium hydroxide solution, reprecipitated by acidification with acetic or hydrochloric acid, and recrystallised from glacial acetic acid. It separates in radiating clusters of flattened needles, decomposing indefinitely at 212° C., insoluble in water, alcohol or benzene, but yielding orange-yellow solutions in alkalis.[2] Other salts of the metals are only sparingly soluble. When heated at 130° to 160° C. with bromine or phosphorus pentabromide the stibinic acid is converted into 1-bromo-3-nitrobenzene.

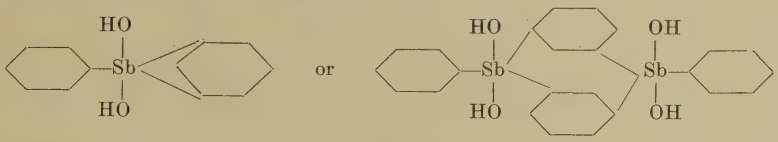
3 : 3′-Diaminodiphenylstibinic acid, $(NH_2.C_6H_4)_2SbO.OH.\frac{1}{2}H_2O$. —3 : 3′-Diaminodiphenylstibinoxide in hydrochloric acid solution is precipitated by ammonium hydroxide and the suspension treated with hydrogen peroxide until a clear solution is obtained. The stibinic acid, formed as the oxidation product, is precipitated by acetic acid. The acid may be purified by conversion to the *stibinic chloride hydrochloride*, which is transformed into the acid by the action of sodium acetate on its aqueous solution.[3] 3 : 3′-Diaminodiphenylstibinic acid is a grey powder, sparingly soluble in alcohol, soluble in warm spirit or warm acetic acid. From its solution in sulphuric acid alcohol precipitates the *sulphate*.

4 : 4′-Diacetylaminodiphenylstibinic acid, $(CH_3.CO.NH.C_6H_4)_2SbO.OH.3H_2O$, may be obtained in two ways : (1) 4 : 4′-Diacetylaminodiphenylstibinoxide, 14 grams, is dissolved in 120 c.c. of methyl alcohol and oxidised by the addition of 50 c.c. of a 3 per cent. hydrogen peroxide solution. The stibinic acid separates out as the reaction proceeds.[4] (2) 2 grams of tri-*p*-acetylaminotriphenylstibine are dissolved in a mixture containing 6 c.c. of 2*N* sodium hydroxide, 30 c.c. of methyl alcohol and 6 c.c. of 3 per cent. hydrogen peroxide. After filtration, the stibinic acid is precipitated by passing in carbon dioxide.

[1] German Patent, 269205; Schmidt, *loc. cit.*
[2] Morgan and Micklethwait, *Trans. Chem. Soc.*, 1911, 99, 2286.
[3] Schmidt, *Annalen*, 1922, 429, 241.
[4] *Ibid.*, p. 138.

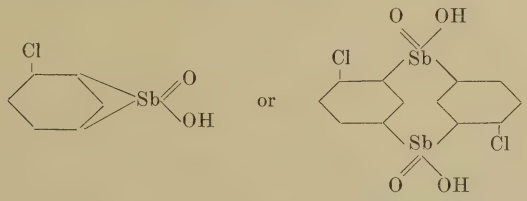
The acid is a colourless powder, melting at about 235° C., slowly soluble in dilute aqueous sodium hydroxide, from which solution it may be reprecipitated by dilute sulphuric or nitric acid, but it is soluble in excess of the precipitant. Hydrochloric acid precipitates the *chloride* from all solutions, and when the acid is boiled with glacial acetic acid the *acetate*, melting at about 205° C., separates out on cooling.

Phenyl-m-phenylenestibinic acid,



Six parts of 3-aminodiphenylstibinoxide are dissolved in a little methyl alcohol by the aid of 21·7 parts of hydrochloric acid (density 1·084), and after dilution with water a solution containing 1·42 parts of sodium nitrite is added. The diazo-solution is then neutralised with sodium hydroxide, when nitrogen is evolved. After completion of the reaction the stibinic acid is precipitated by acidification. The crude acid is collected, dissolved in warm alcoholic hydrochloric acid, reprecipitated by water and extracted with ether. The ether solution is shaken with dilute sodium hydroxide solution, and then separated and treated with ammonium chloride, when the stibinic acid is precipitated. In the dried condition the acid is a pale brown powder, decomposing when heated, without any definite melting-point ; it is only sparingly soluble in alkali, but readily soluble in warm acetic acid.[1]

Chloro-m-phenylenestibinic acid,



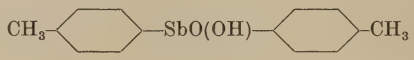
3-Amino-4-chlorophenylstibinous chloride, 32 parts, is dissolved in 400 parts of water containing 133 parts of hydrochloric acid (density 1·084) and diazotised by 7·3 parts of sodium nitrite, when a sparingly soluble diazo-compound separates. Ice is added and the liquor well stirred whilst 200 parts of sodium hydroxide (density 1·19) are run in. A violent evolution of nitrogen takes place and when the reaction has subsided the mixture is filtered and the acid precipitated by acidification with hydrochloric acid. The acid is collected, dried, and dissolved in warm alcoholic hydrochloric acid containing animal charcoal, from which solution, after cooling, the acid is reprecipitated by dilution with water. Final purification is effected by solution in alkali and reprecipitation by acid. The acid thus obtained is a brown powder, which does not reduce Tollen's silver solution, and is only slowly soluble in cold caustic alkali, more readily soluble on warming ; in most organic solvents it is insoluble. The acid decomposes without melting on heating.[2]

[1] German Patent, 269205. The dimeric formula given is based on the dimeric formula given in this patent for chloro-*m*-phenylenestibinic acid.

[2] German Patent, 269205.

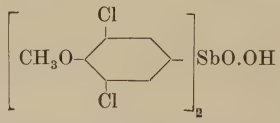
Benzidine yields 4-hydroxydiphenylstibinic acid and not the distibinic acid when diazotised *p*-aminophenylstibinic acid is coupled with it.[1]

Di-p-tolylstibinic acid,



This acid may be prepared by two methods :[2] (1) Tri-*p*-tolylstibine, 9 grams, is suspended in 150 c.c. of methyl alcohol and mixed with another 30 c.c. of methyl alcohol which has previously been saturated with hydrogen chloride. The mixture, through which a current of carbon dioxide is passed, is boiled on the water-bath, and after about 15 minutes a clear solution results. After boiling for $1\frac{1}{4}$ hours the liquid is cooled and made distinctly alkaline with dilute aqueous sodium hydroxide. The white precipitate which separates is removed as a suspension in ether and added to the solid obtained from the aqueous layer by precipitation with acetic acid. The product is recrystallised from alcohol. (2) A solution of 6 grams of tri-*p*-tolylstibine in acetone is gradually added to a boiling mixture of 113 c.c. of water, 37 c.c. of 5*N* sodium hydroxide and 22·5 c.c. of 6 per cent. hydrogen peroxide. The solution, filtered from a slight precipitate, is treated with dilute sulphuric acid and the voluminous white precipitate obtained is partly dried, washed with warm alcohol, and recrystallised from benzene. The acid is a white amorphous product, sintering at 230° C. and melting at 260° C. It is slightly soluble in hot or cold alcohol or cold benzene and readily soluble in hot benzene.

3 : 3′ : 5 : 5′-Tetrachloro-4 : 4′-dimethoxydiphenylstibinic acid,



This acid occurs when the corresponding stibinic chloride is hydrolysed. It is a white amorphous powder, melting with decomposition at 228° to 229° C. In the usual solvents it is insoluble, but it slowly dissolves in warm dilute sodium hydroxide. Alcoholic hydrochloric acid reconverts it into the chloride.[3]

Di-biphenylstibinic acid,[4]

is a white amorphous powder, isolated from the trichloride by the action of alcoholic ammonia. It softens above 201° C. and melts with decomposition at 204° to 205° C.

[1] Riddell and Basterfield, *Trans. Roy. Soc. Canada*, 1929, [iii], **23**, III, 45.
[2] Goddard and Yarsley, *J. Chem. Soc.*, 1928, p. 721.
[3] Löloff, *Ber.*, 1897, **30**, 2840.
[4] Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2046.

Stibino-compounds.

The stibino-compounds may be obtained as follows :—

(1) By reduction of the corresponding stibinic acids :

$$2RSbO(OH)_2 + 4H_2 \longrightarrow RSb=SbR + 6H_2O$$

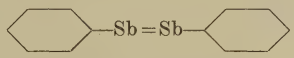
(2) By reducing stibinoxides or dichlorostibines :

$$2RSbO + 2H_2 \longrightarrow RSb=SbR + 2H_2O$$
$$2RSbCl_2 + 2H_2 \longrightarrow RSb=SbR + 4HCl$$

The products thus obtained readily undergo oxidation, concentrated nitric acid causing them to explode. Since mineral acids cause the bases to undergo decomposition, it is necessary in the case of aryl-dichlorostibines that an excess of alkali hypophosphite be present to counteract the effect of the free acid formed. The compounds RSb=SbR are dark solids, dissolving in acids giving unstable solutions.

A number of interesting compounds are also known which possess the grouping —As=Sb—. The compounds RSb=SbR′ tend to be yellow, but substitution of arsenic for one of the antimony atoms, RAs=SbR′, produces orange to yellowish-brown derivatives.

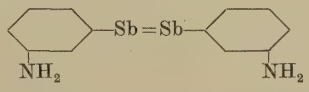
Stibinobenzene,



Two methods may be used for isolating this derivative : (1) 4 grams of phenylstibinoxide in 80 c.c. of acetic acid and 80 c.c. of acetone are treated with 12 grams of sodium hypophosphite in 15 c.c. of acetic acid at 65° C. After 2 to 3 hours the brown precipitate which is formed is washed with methyl alcohol to remove acetic acid and immediately dried in a vacuum desiccator.[1] (2) To a solution of 5 parts of phenyl-stibinic acid in the calculated quantity of dilute sodium hydroxide 10 parts of sodium hydrosulphite in aqueous solution are added with stirring. The mixture is then warmed at 30° C. for several hours, the stibino-compound separating as a yellow precipitate, which finally becomes brown. The product is collected, dried, and freed from impurities by boiling with a mixture of equal parts of benzene and alcohol and a little copper powder for several hours. The mixture is then filtered and the solvents distilled off, the stibino-compound being obtained as a pale yellow powder.[2]

Stibinobenzene darkens and sinters at about 160° C., finally yielding a black mass. It is insoluble in water, but dissolves in glacial acetic acid and may be recrystallised from chloroform. Oxidation readily takes place in air, fuming nitric acid oxidises the compound explosively, and hydrogen peroxide in acetic acid solution converts it into phenylstibinic acid.

3 : 3′-Diaminostibinobenzene,

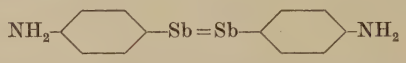


[1] Schmidt, *Annalen*, 1920, **421**, 221.
[2] German Patent, 268451.

Three processes have been evolved for the preparation of this compound : (1) 3-Aminophenyldichlorostibine hydrochloride, 3·2 grams, is made into a paste with 10 c.c. of water and treated with a solution of 10 grams of sodium hypophosphite in 25 c.c. of water and 10 c.c. of hypophosphorous acid (density 1·15), the operation being conducted at a temperature of 50° C. in an atmosphere of carbon dioxide. When the reaction is complete the solution is cooled, a salt of the base separating out. This is dissolved by the addition of water and the solution poured into dilute soda solution, when dark brown flocks of the base are precipitated.[1] (2) 3-Aminophenyldichlorostibine hydrochloride, 128 parts, is dissolved in 2000 parts of water containing 64 parts of sodium hydroxide. To the solution is added a filtered solution prepared from 100 parts of sodium hydrosulphite and 50 parts of magnesium chloride in 1000 parts of water and 100 parts of 10 per cent. sodium hydroxide solution. After a short time a yellow precipitate commences to separate, the rate of deposition being increased if the solution be warmed. After several hours the thick orange-yellow paste is filtered off and washed successively with water, dilute sodium hydroxide solution, then water again, and dried.[2] (3) 3-Aminophenyldichlorostibine hydrochloride, 32 parts, in 1000 parts of water, is treated with a saturated solution of 70 parts of sodium hypophosphite. An excess of hypophosphite is used to counteract the tendency of the mineral acid produced to decompose the base. The mixture is rapidly heated to about 100° C., and poured into ammoniacal ice-water, when the stibino-compound is precipitated. The reduction may also be effected in methyl alcohol solution.

3 : 3′-Diaminostibinobenzene is a dark brown powder, sintering above 120° C. and forming a black mass. It dissolves rapidly in hydrochloric acid, excess of which precipitates a light brown *dihydrochloride*. Solutions in glacial acetic acid soon become brown. With sulphuric acid a *sulphate* is produced. If an hydrochloric acid solution of the base be allowed to stand, decomposition gradually takes place, metallic antimony separating out. The base rapidly oxidises in air and explodes when treated with nitric acid (density 1·49). Solutions in tartaric acid may be reprecipitated by alcohol, this affording a method for purifying the base. The base is converted by acetic anhydride into *3 : 3′-diacetamidostibinobenzene*, a yellow powder, insoluble in water and organic solvents.[3]

4 : 4′-Diaminostibinobenzene,[4]



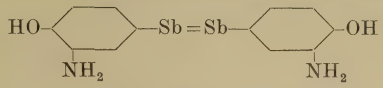
is obtained by reducing 4-nitrophenylstibinic acid with sodium hyposulphite.

1-Stibinonaphthalene is similarly obtained from α-naphthylstibinic acid.

4 : 4′-Carboxymethylstibinobenzene has been isolated only in an impure state.

[1] Schmidt, *loc. cit.*
[2] German Patent, 268451.
[3] German Patent, 284231.
[4] Riddell and Basterfield, *Trans. Roy. Soc. Canada*, 1929, [iii], **23**, III, 45.

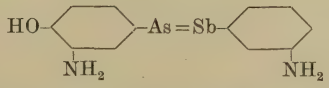
3 : 3′-Diamino-4 : 4′-dihydroxystibinobenzene,



This compound is the *analogue of* "*salvarsan*" and is prepared as follows: (1) 3-Amino-4-hydroxyphenyldichlorostibine hydrochloride, 2·2 grams, is treated with 4 c.c. of acetic acid and 7 c.c. of water, followed by a solution of 6·6 grams of sodium hypophosphite in 18 c.c. of water and 6·6 c.c. of hypophosphorous acid (density 1·15). The mixture is rapidly filtered and warmed at 30° C. for 45 minutes, the operation being conducted in an atmosphere of carbon dioxide. A red solid separates, and after several hours cooling in ice, the product is filtered off and dried. The substance obtained is a phosphite or hypophosphite of the base, and when dissolved in alkali or ammonium hydroxide is decomposed on the addition of ammonium chloride with liberation of the free base. The product thus obtained is washed and dried *in vacuo*.[1] (2) 3-Nitro-4-hydroxyphenylstibinic acid is dissolved in the solution from 6 parts of sodium hydroxide in 500 parts of water and mixed with a solution containing 200 parts of anhydrous sodium hydrosulphite in 400 parts of water containing 17 parts of sodium hydroxide. The red solution obtained slowly decolorises and a precipitate separates which redissolves on the addition of more sodium hydroxide. The liquid is now heated at 40° C. for several hours, when 3 : 3′-diamino-4 : 4′-dihydroxystibinobenzene commences to separate as a reddish-brown precipitate. When no further deposition is observed, the solid is filtered off and washed in the absence of air.

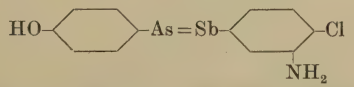
The stibino-compound is a dark brown powder, very readily oxidised and exploding when treated with nitric acid (density 1·49). It is soluble in dilute sodium hydroxide or acids, the solutions being unstable. The *dihydrochloride* is precipitated from a solution in dilute hydrochloric acid by adding concentrated hydrochloric acid, and sulphates precipitate an *acid sulphate* from solutions of the hydrochloride. Alkaline hydrogen peroxide converts the stibino-compound into 3-amino-4-hydroxyphenylstibinic acid. The hydroxyl-group is detected by means of ferric chloride, and the amino-group by diazotisation and coupling. The base is also readily acetylated, and it condenses with aldehydes.

3 : 3′-Diamino-4-hydroxyarsenostibinobenzene,[2]



This derivative is formed by condensing 3-amino-4-hydroxyphenylarsine with 3-aminophenylstibinous oxide. It is a brown powder, insoluble in water, soluble in aqueous sodium hydroxide, giving a brownish-red solution in which oxidising agents cause scission of the molecule. Hydrogen chloride reacts to form a *dihydrochloride*.

4′-Chloro-3′-amino-4-hydroxyarsenostibinobenzene,

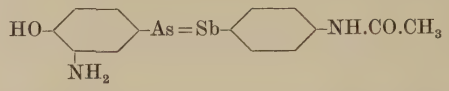


[1] Schmidt, *Annalen*, 1920, 421, 151.

[2] German Patent, 396697.

is the condensation product of 3-amino-4-chlorophenylstibinous oxide and 4-hydroxyphenylarsine. It forms a reddish-brown mass, which gives a *hydrochloride* as an orange-yellow powder, fairly stable in air.

3-Amino-4′-acetamido-4-hydroxyarsenostibinobenzene,

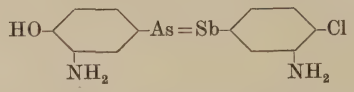


from 3-amino-4-hydroxyphenylarsine and 4-acetamidophenylstibinous oxide, is a brown powder, soluble in dilute acid or alkali.

3-Amino-4-hydroxyphenylarsine also reacts with potassium antimonyl tartrate in aqueous alkali solution to form a dark brown arsenic-antimony compound, soluble in acid or alkali.[1] This body yields a N-*hydroxybenzylidene derivative* when shaken with salicyl aldehyde.

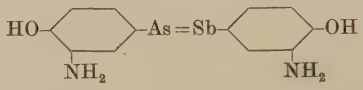
4-Hydroxyphenylarsine in aqueous sodium hydroxide reacts with an alkaline antimony solution, prepared from antimony trichloride with the addition of glycerol, to form a dark brown arsenostibino-compound, soluble in dilute alkali, insoluble in dilute acid.

4′-Chloro-3 : 3′-diamino-4-hydroxyarsenostibinobenzene,



is the condensation product of 3-amino-4-hydroxyphenylarsine and 3-amino-4-chlorophenylstibinous chloride in dilute aqueous hydrochloric acid solution.[2]

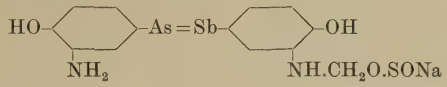
3 : 3′-Diamino-4 : 4′-dihydroxyarsenostibinobenzene,[3]



This compound is of interest since it resembles " salvarsan " in structure, the difference being that one arsenic atom is here replaced by antimony. Two solutions are prepared to isolate this compound. The first consists of 12·8 grams of 3-nitro-4-hydroxyphenylarsinic acid in 300 c.c. of water and 8·5 c.c. of 40 per cent. sodium hydroxide, heated to 45° C. The second solution is similar to the first, but 15 grams of 3-nitro-4-hydroxyphenylstibinic acid replace the arsinic acid. These solutions are simultaneously added to 300 grams of sodium hydrosulphite in 1700 c.c. of cold water, the mixture being stirred during the operation. The temperature is gradually raised to 68° C., when the base separates out and after 1·5 hours is filtered off in an inert atmosphere, washed with water and finally with methyl alcohol. The base when dry is insoluble in neutral solvents. The *dihydrochloride* is prepared by suspending the base in methyl alcohol and adding 12 c.c. of a 29 per cent. solution of methyl alcoholic hydrogen chloride. The solution after filtration is poured into dry ether or concentrated hydrochloric acid, when the salt separates. It is a brownish-yellow amorphous powder, soluble in water, the solution having an acid reaction. Sodium hydroxide

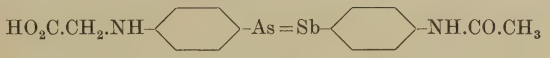
[1] German Patent, 397275.
[2] Schmidt, *Annalen*, 1920, 421, 232.
[3] American Patent, 1422294.

reprecipitates the base, which is soluble in excess of precipitant. The *sodium sulphoxylate derivative* of the base,



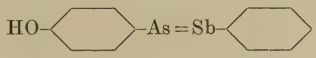
is formed by dissolving 1·9 grams of the dihydrochloride in 6 c.c. of methyl alcohol and adding 2 c.c. of a 37·5 per cent. solution of sodium sulphoxylate. The mixture is neutralised with sodium carbonate, filtered and poured into 400 c.c. of anhydrous alcohol-ether (1 : 1). The precipitated product is dried *in vacuo*. It is obviously impossible to ascertain in which amino-group the substitution has occurred.

4′-Acetamidophenylstibinoarseno-4-phenylglycine,[1]



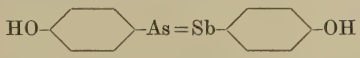
This derivative results when 14 grams of phenylglycine-*p*-arsinic acid in 200 c.c. of water and 100 c.c. of normal sodium hydroxide solution are mixed with 15·2 grams of 4-acetamidophenylstibinic acid in 300 c.c. of water and 50 c.c. of sodium hydroxide, and the whole reduced with sodium hydrosulphite. The product is brownish-black, soluble in aqueous alkalis or aqueous pyridine, but insoluble in water, alcohol or acetone.

4-Hydroxyphenylarsenostibinobenzene,[2]



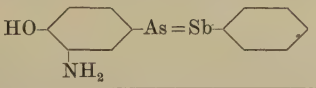
Phenylstibinoxide, 2·13 grams, is dissolved in 100 c.c. of hot acetic acid and a methyl alcohol solution of 1·7 grams of 4-hydroxyphenylarsine added. After boiling for a short time the solution is poured into ether, the required compound being precipitated as a brown powder, soluble in alkalis.

4 : 4′-Dihydroxystibinoarsenobenzene,[3]



Solutions containing, respectively, 12 grams of sodium 4-hydroxyphenylarsinate in 240 c.c. of water and 13·2 grams of 4-hydroxyphenylstibinic acid in 30 c.c. of water and 50 c.c. of normal sodium hydroxide, are mixed together and diluted with 1250 c.c. of water. To this solution 250 grams of sodium hydrosulphite are added and the whole stirred until no further precipitate separates, the operation being completed in about two hours. The product is then filtered off, washed with water and dried in a vacuum. It is a brownish-black powder, insoluble in water, soluble in alcohols, acetone, pyridine and aqueous sodium hydroxide.

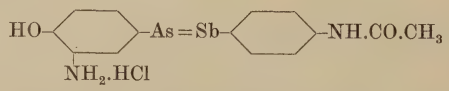
3-Amino-4-hydroxyphenylarsenostibinobenzene,[4]



[1] German Patent, 270255. [2] German Patent, 269744. [3] German Patent, 270255.
[4] German Patents, 269743, 270255, 270259; Ehrlich and Karrer, *Ber.*, 1913, 46, 3564.

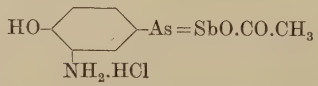
This derivative may be prepared by either of the following methods: (1) 3-Amino-4-hydroxyphenylarsine, 1·9 grams, is dissolved in 30 c.c. of methyl alcohol and about 1 c.c. of 10*N* alcoholic hydrochloric acid added, oxygen being excluded. To the solution 2·7 grams of phenyldichlorostibine in methyl alcohol are added, and 500 c.c. of ether stirred into the mixture. The *hydrochloride* of the required base separates out as a brown amorphous powder, which is washed with ether and dried *in vacuo*. (2) 10 grams of 3-amino-4-hydroxyphenylarsenoxide in 60 c.c. of methyl alcohol, 200 c.c. of water and 50 c.c. of normal sodium hydroxide solution are mixed with 12·3 grams of phenylstibinic acid in 300 c.c. of water and 50 c.c. of normal sodium hydroxide. The mixture is then treated with 200 grams of sodium hydrosulphite and 40 grams of magnesium chloride in 1000 c.c. of water and the whole stirred at room temperature until a test portion remains clear on warming. The precipitate is filtered off, washed with water and dried *in vacuo*, the yield being quantitative. The product is a brownish-yellow powder, readily soluble in pyridine, aqueous alkalis and methyl alcohol. The *hydrochloride* yields a yellowish-brown *addition product* with *gold chloride*, and a brownish-green *compound* with *osmium chloride*, these being soluble in water but insoluble in ether.

3 - Amino - 4 - hydroxyphenylarseno - 4′ - acetamidostibino - benzene hydrochloride,[1]



This compound is obtained in brown flocks when 1·64 grams of 4-acetamidophenyldi-iodostibine [2] in 40 c.c. of acetic acid are treated with 0·8 gram of 3-amino-4-hydroxyphenylarsine in alcoholic hydrochloric acid and the whole diluted with ether. It is readily soluble in water or methyl alcohol, and gives a clear solution in alkalis.

3-Amino-4-hydroxyphenylarsenoantimonious acetate hydrochloride,[3]



This is the condensation product of 3-amino-4-hydroxyphenylarsine (2 grams), in a little methyl alcohol, with a hot solution of 3·6 grams of tartar emetic in acetic acid. After boiling for a minute, brownish-yellow flocks separate, which are easily soluble in water, alkalis or dilute hydrochloric acid. From the latter solution sulphuric acid precipitates a sparingly soluble *sulphate*, and dimethylaminobenzaldehyde a sparingly soluble *Schiff's base*.

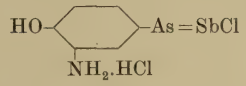
4-Acetamidophenylarsenoantimonious bromide,[4]

4-Acetamidophenylarsine (0·6 part), obtained by the reduction of 4-acetamidophenylarsinic acid with zinc dust and hydrochloric acid, is dissolved in 50 c.c. of methyl alcoholic hydrochloric acid and 1·08 parts

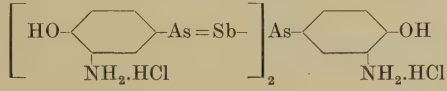
[1] Ehrlich and Karrer, *Ber.*, 1913, 46, 3564.
[2] German Patent, 214428.
[3] German Patent, 269744.
[4] German Patent, 269743.

of antimony tribromide in 25 c.c. of methyl alcohol added. On pouring into ether, a reddish-brown powder of the constitution indicated is precipitated. It is soluble in water and dilute hydrochloric acid.

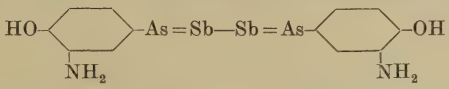
3 - Amino - 4 - hydroxyphenylarsenoantimonious chloride hydrochloride,[1]



A solution of 1 gram of 3-amino-4-hydroxyphenylarsine in methyl alcohol is mixed with a similar solution of 1·23 grams of antimony trichloride. After adding 0·88 gram of crystalline cupric chloride in methyl alcohol, the required compound is precipitated in the form of its *cupric chloride addition compound* by the addition of ether. For the product obtained when the preparation is carried out in methyl alcohol solution containing hydrochloric acid, the following formula has been suggested, but it is not supported by analysis : [2]

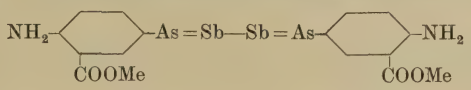


Bis-3-amino-4-hydroxyphenylarsenoantimonide,[3]



A solution of 23·3 grams of 3-amino-4-hydroxyphenylarsinic acid in 400 c.c. of water and 60 c.c. of 2*N* sodium hydroxide solution is mixed with 33·2 grams of tartar emetic in 650 c.c. of water. The mixture is then added to a solution of 500 grams of sodium hydrosulphite and 100 grams of magnesium chloride in 2500 c.c. of water and the whole well stirred at 50° to 55° C. until a test portion remains clear on warming. The precipitate is then filtered off, washed and dried in a vacuum. It is a reddish-brown powder, giving clear solutions in dilute hydrochloric acid and aqueous sodium hydroxide.

Bis-4-amino-3-carbomethoxyphenylarsenoantimonide,[4]



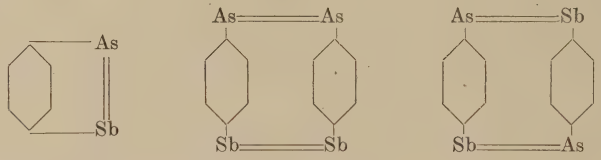
results when antimonyl chloride is condensed with methyl anthranilylarsine in acetic acid solution. It is a brown powder, sparingly soluble in water or methyl alcohol.

4-Arsinophenylstibinous oxide or *Phenyl-1-arsenoxide-4-stibinoxide,*[5]

occurs as a colourless powder when the corresponding acid is reduced with sulphur dioxide in the presence of a trace of iodine in methyl alcoholic hydrogen chloride solution. Reduction in the absence of

[1] German Patent, 270259. [2] Ehrlich and Karrer, *loc. cit.*
[3] German Patent, 270255. [4] German Patent, 269744. [5] German Patent, 397151.

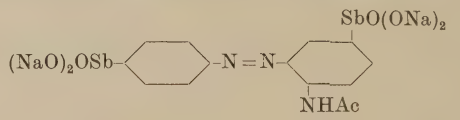
iodine gives an intermediate product. Reduction of the oxide by phosphorous acid in acetic-hydrochloric acid solution in the presence of iodine gives a pale yellow reduction product. This might have any of the structures



Phenylarsinic acid-stibinic acid is reduced by sodium hyposulphite to a dark brown product. Reduction of 4-hydroxyphenyl-1-arsinic acid-3-stibinic acid, $HO.C_6H_3(SbO_3H_2)(AsO_3H_2)$, by stannous chloride and concentrated hydrochloric acid in the presence of a trace of iodine, yields an orange-yellow solid, probably *4-hydroxyphenylstibinearsine.*

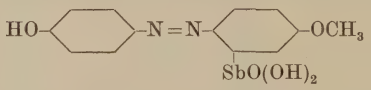
Azo-compounds.

Sodium 2-acetamidoazobenzene-5 : 4′-distibinate,[1]



occurs when diazotised *p*-aminophenylstibinic acid is coupled with sodium *p*-acetamidophenylstibinate in alkaline solution.

4-Hydroxybenzeneazo-4′-methoxyphenyl-2′-stibinic acid,[2]



is prepared from 3-methoxy-6-acetamidophenylstibinic acid by hydrolysis, diazotisation and coupling with phenol.

Azobenzene-p-stibinic acid,

is isolated by diazotising and " stibinating " *p*-aminoazobenzene.

Arsinicstibinic Acids.

p-Phenylenearsinicstibinic acid, $[\{C_6H_4(AsO_2)(SbO_2).H_2O\}.4H_2O]_x$.—*p*-Aminophenylarsinic acid, 21·7 grams, is dissolved in 100 c.c. of water and 60 c.c. of 5*N* hydrochloric acid and diazotised. To the diazo-solution is added successively 34 grams of tartar emetic in 200 c.c. of water and 120 c.c. of 5*N* ice-cold sodium hydroxide. Nitrogen is evolved and the reaction is complete when a test portion no longer couples with R-salt. Acidification with dilute hydrochloric acid then precipitates the crude acid, which is freed from antimony trioxide by stirring the moist paste with 200 c.c. of 5*N* hydrochloric

[1] Brahmachari and Gupta, *J. Asiatic Soc. Bengal*, 1929, **25**, 301.
[2] Riddell and Basterfield, *Trans. Roy. Soc. Canada*, 1929, [iii], **23**, III, 45.

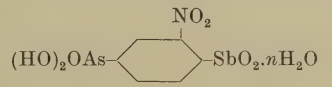
acid, filtering and washing with similar acid until a test portion of the filtrate on dilution is not orange-red when treated with hydrogen sulphide. The acid may be further purified by forming a paste with 200 c.c. of hydrochloric acid (density 1·19), the product soon dissolving. Charcoal is added, the mixture filtered and the filtrate stirred with 20 c.c. of pyridine and 75 c.c. of hydrochloric acid (density 1·19), when the pyridine double salt separates. This is filtered off, decomposed by water, the solution filtered and the solid dissolved in sodium hydroxide. The addition of dilute hydrochloric acid then precipitates pure *p*-phenylenearsinicstibinic acid. This is removed, washed and dried at the ordinary temperature, then stirred several times with water, washed and dried in air until constant in weight. The acid may also be obtained by treating diazotised stibanilic acid (*p*-aminophenylstibinic acid) with alkaline arsenite.

From the first method of preparation about 25 grams of colourless powder are isolated. This gives white fumes and a cacodyl-like odour when heated on platinum foil. It is not soluble in the usual solvents, but dissolves readily in alkalis and concentrated hydrochloric acid. Like the primary stibinic acids it exhibits the phenomenon of gradual neutralisation with alkali hydroxide, the rate of neutralisation depending on the concentration of the hydroxyl ions, the temperature and the particular cation. The steps in the process of neutralisation are not sufficiently sharply differentiated to allow conclusions to be drawn as to the degree of polymerisation of the compound.[1] *Ammonium chloride* in hydrochloric acid solution reacts with the acid to form the *compound* $[H_2O_3As.C_6H_4.Sb(OH)Cl_3]_3[NH_3]_2.6H_2O$, a white, crystalline product, insoluble in the usual organic solvents, only decomposed by water with difficulty and soluble in an excess of dilute sodium hydroxide solution. *Pyridine hydrochloride* reacts with the arsinicstibinic acid to form the *compound* $(H_2O_3As.C_6H_4.SbCl_4)_2(C_5H_5N.HCl)_3.1\frac{1}{3}H_2O$.

4-Hydroxyphenylene-1-arsinic acid-3-stibinic acid, $[\{HO.C_6H_3(AsO_2)(SbO_2).H_2O\}.3H_2O]_x$.—This is formed by the diazotisation of 3-amino-4-hydroxyphenylarsinic acid and treatment of the product with tartar emetic in alkaline solution. The acid is purified by the methods adopted for the preceding acid, which the present compound resembles in properties.

The analysis of these compounds is effected by boiling them with a mixture of concentrated sulphuric acid and nitric acid (density 1·49) and subsequent treatment of the solution with ammonium sulphate until all the residual nitric acid has been destroyed. The arsenic and antimony are then estimated in the usual manner.

3-Nitrophenylene-1-arsinic acid-4-stibinic acid,

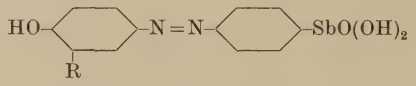


3-Nitro-4-aminophenylarsinic acid is diazotised and treated with tartar emetic in neutral or slightly acid solution. The resulting product is a brown powder.[2]

[1] Schmidt, *Ber.*, 1924, 57, [B], 1142.
[2] German Patent, 296940.

Azo-dyes containing Antimony.[1]

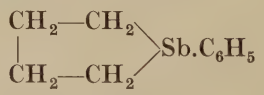
These dyes are prepared by the diazotisation and coupling of *p*-aminophenylstibinic acid (stibanilic acid). The powdered products are mostly of brown shades and all are insoluble in water, alcohol, acetone, chloroform and benzene, sparingly soluble in phenol, but readily soluble in sodium and ammonium hydroxides. They do not melt and are not decomposed at 250° C. The disodium salts are obtained in solid form as brown scales, dilute solutions of which in water range from deep orange-brown to yellow-brown. The solutions dye wool a light orange-yellow. The compounds are perfectly stable over a period of six months, and are unaffected by light or heat. The salts are insoluble in most organic solvents, but are fairly soluble in water-alcohol mixtures, precipitating on long standing. The following azo-dyes are known, the compound with which the diazotised *p*-aminophenylstibinic acid is coupled being shown in brackets : *4-hydroxyazobenzene-4′-stibinic acid* (phenol) ; *4-hydroxy-2-chloroazobenzene-4′-stibinic acid* (*o*-chlorophenol) ; *4-hydroxy-3-nitroazobenzene-4′-stibinic acid* (*o*-nitrophenol) ; *4-hydroxy-3-aminoazobenzene-4′-stibinic acid* (*o*-aminophenol) ; *4-hydroxy-3-methylazobenzene-4′-stibinic acid* (*o*-cresol) ; *4-hydroxy-3-carboxyazobenzene-4′-stibinic acid* (salicylic acid). The use of pyrocatechol does not give the expected product. The general formula of the compounds may be represented thus :



p-Aminophenylstibinic acid has also been diazotised and coupled with the following compounds, the colour of the dye being indicated : [2] *Dimethylaniline* (brown), *diethylaniline* (purple), *α-naphthol-4-sulphonic acid* (dark red), *2 : 5-aminonaphthol-7-sulphonic acid* (light reddish-brown), *2-naphthylamine-3 : 6-disulphonic acid* (dark brown), *1 : 8-aminonaphthol-3 : 6-disulphonic acid* (sodium salt purple), *2-naphthol-3 : 6-disulphonic acid* (sodium salt orange-brown), and *1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid* (sodium salt purple).

Heterocyclic Compounds containing Antimony.

Phenylcyclotetramethylenestibine,

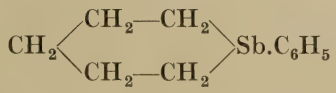


To the magnesium compound from 50 grams of 1 : 4-dibromobutane in 200 c.c. of anhydrous ether, 40 grams of phenyldichlorostibine dissolved in 3 volumes of dry ether are slowly added, the mixture being well cooled and stirred, and the operation conducted in an inert gas.[3] Fractionation of the resulting product after decomposition gives 15 grams of the stibine, B.pt. 156° to 158° C. at 20 to 22 mm., n_D 1·6313 and $n_F - n_C$ 0·02737 at 23° C.

[1] Dunning and Reid, *J. Amer. Chem. Soc.*, 1926, 48, 2959.
[2] *Ibid.*, 1927, 49, 2869.
[3] Grüttner and Krause, *Ber.*, 1916, 49, 437.

It is a colourless, somewhat viscous oil, of unpleasant odour, and becomes cloudy even in the presence of traces of oxygen. When dry chlorine is passed into its solution in carbon tetrachloride and the solvent removed, the *dichloride* is obtained as colourless crystals, M.pt. 150° C. The *dibromide*, prepared in a similar manner, yields colourless needles, M.pt. 149° C.

Phenylcyclopentamethylenestibine,

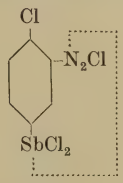


This occurs when the 1 : 4-dibromobutane in the preceding preparation is replaced by 1 : 5-dibromopentane, and 75 grams of phenyldichlorostibine yield about 37 grams of the pure stibine. It is a colourless viscous oil of faint unpleasant odour, boiling at 169° to 171° C. at 18 to 20 mm., density 1·4966 at 20° C., n_D 1·6203 and $n_F - n_C$ 0·02412 at 22·4° C. It dissolves in ether, benzene and carbon tetrachloride, is fairly soluble in hot alcohol, sparingly soluble in water. With ethyl iodide and mercuric chloride no addition products are formed, but atmospheric oxygen converts it in a few hours to *phenylcyclopentamethylenestibine oxide*, $C_5H_{10}.Sb(C_6H_5) : O$, a colourless powder, unmelted at 280° C., soluble in alcohol, insoluble in petroleum ether. The stibine also yields a *dichloride*, which is a white crystalline powder, M.pt. 141° to 142° C.

Derivatives of pyridine, quinoline or *iso*quinoline may be prepared by causing the diazotised amino-compounds of such substances to react with antimonites or the corresponding free acids. The parent material may contain substituents, *e.g.* hydroxy-, amino-, carboxy- or phenyl- radicals or halogens. The most advantageous proportions appear to be 2 to 3 molecular equivalents of antimonite to each equivalent of heterocyclic compound. Reduction with suitable agents produces stibino-compounds.[1]

Benzenediazonium Chloride-Antimony Chloride Internal Complex Salts.[2]

p-Chloro-m-amino-benzenediazonium chloride-antimony chloride complex salt,



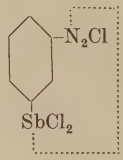
p-Chloro-*m*-aminophenyldichlorostibine hydrochloride, 7 grams, is dissolved in about 20 c.c. of methyl alcohol and cooled in ice. Treatment with 40 c.c. of 5*N* hydrochloric acid, followed by 30 c.c. of normal sodium nitrite solution, causes the separation of a deep yellow to orange-yellow microcrystalline precipitate. After standing for five minutes

[1] English Patent, 250287 (1924).

[2] Schmidt and Hofmann, *Ber.*, 1926, **59**, [B], 555.

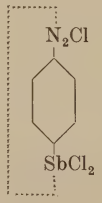
in ice, this product is collected, washed with ice-cold 5*N* hydrochloric acid and dried *in vacuo* over caustic alkali and sulphuric acid. About 7 grams of orange-yellow powder result, which is about 100 per cent. yield. A somewhat purer product is isolated if an ice-cold solution of 7 grams of the stibine hydrochloride in 50 c.c. of methyl alcohol are treated with an ice-cold solution of 7 c.c. of amyl nitrite in 30 c.c. of acetic acid; the orange-yellow body immediately separates and is filtered, washed with acetic acid and dried. The complex salt decomposes at about 100° C. and explodes with evolution of fumes of antimony oxide when heated on platinum foil. It cannot be further purified by recrystallisation. In dry ether or benzene it is insoluble, and its solution in methyl or ethyl alcohol decomposes with evolution of nitrogen even in the cold. Water, aqueous sodium acetate, dilute hydrochloric acid and acetic acid cause decomposition in the cold, and alkali solutions cause energetic nitrogen evolution. Alkali-soluble stibinic acids are formed in the latter case.

m-Amino-benzenediazonium chloride-antimony chloride complex salt,



Owing to the sparing solubility of *m*-aminophenyldichlorostibine hydrochloride, the preparation of the diazo-compound is accomplished as follows: 7 grams of the hydrochloride are stirred with powdered ice and 15 c.c. of 5*N* sodium hydroxide solution, when a yellow precipitate of the oxide separates. This is rapidly brought into solution by 50 c.c. of 5*N* ice-cold hydrochloric acid and diazotised by 30 c.c. of normal sodium nitrite solution. The precipitated diazo-compound is immediately collected and washed with ice-cold 5*N* hydrochloric acid (20 c.c.). The product readily decomposes, so that only small quantities are dried. It decomposes at 165° to 167° C. An alternative method of preparation consists of treating 16 grams of *m*-aminophenyldichlorostibine hydrochloride in 250 c.c. of methyl alcohol and 30 c.c. of acetic acid with 8 grams of amyl nitrite. Alkali decomposes the complex with evolution of nitrogen and formation of stibinic acids.

p-Benzenediazonium chloride-antimony chloride complex salt,

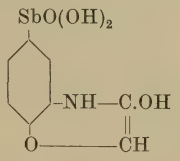


This may be prepared by methods similar to the foregoing. The acetic acid in the second method of preparation is replaced by saturated methyl alcoholic hydrogen chloride. The product is very unstable and reacts with alkali in the usual manner.

Derivative of 1 : 4-Benzisoxazine.[1]

A considerable amount of research has been carried out on the arsenical derivatives of 1 : 4-benzisoxazine,[2] and the present compound appears to be the beginning of similar work on antimonials.

3-Hydroxy-1 : 4-benzisoxazine-6-stibinic acid,

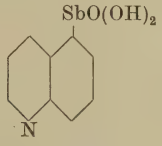


6-Amino-3-hydroxy-1 : 4-benzisoxazine hydrochloride (12 grams), when subjected to the Bart-Schmidt reaction, yields 1·25 grams of the stibinic acid as a light brown amorphous powder, insoluble in water and the usual solvents, but readily soluble in dilute alkali solutions.

Antimony Compounds of the Quinoline Series.[3]

The general method of preparation for these compounds is as follows: The aminoquinoline (6 grams or $\frac{1}{24}$ gram-molecule) in 50 c.c. of water and 20 c.c. of hydrochloric acid is diazotised at 0° C. by 3 grams of sodium nitrite. The diazo-solution is added slowly, with simultaneous addition of 20 c.c. of 6*N* sodium hydroxide, to an ice-cold solution prepared from 12·6 grams of antimony trichloride, 20 c.c. of 5*N* hydrochloric acid and 20 c.c. of glycerol, the resulting mixture being treated with 6*N* sodium hydroxide until the precipitate which forms just redissolves, after which the whole is diluted to 800 c.c. After standing overnight the solution is filtered and the filtrate acidified with acetic acid. The resulting precipitate is suspended in 50 c.c. of concentrated hydrochloric acid, the product collected after one hour and washed with concentrated hydrochloric acid. The stibinic chloride thus obtained free from antimony oxide is decomposed by excess of dilute alkali and the stibinic acid precipitated by acetic acid.

Quinoline-5-stibinic acid,



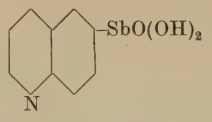
is a buff powder, very sparingly soluble in most solvents, although moderately easily soluble in glacial acetic acid and readily soluble in dilute acids or alkalis. The analysis corresponds to the formula $C_9H_6O_2NSb.H_2O$. The *sodium salt* is readily soluble in water. When the acid in dilute hydrochloric acid is treated at 0° C. with concentrated hydrochloric acid, a buff microcrystalline powder results; this is *quinoline-5-stibinic chloride hydrochloride*, M.pt. 222° C.

[1] Balaban, *J. Chem. Soc.*, 1930, p. 1685.

[2] See this Volume, Part II, p. 427.

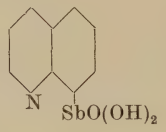
[3] Morgan and Cook, *J. Chem. Soc.*, 1930, p. 743. These compounds are similar to those described for arsenic in this Volume, Part II, p. 419.

Quinoline-6-stibinic acid,

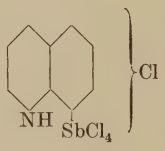


containing a molecule of water, is a buff powder, moderately soluble in methyl alcohol and readily soluble in dilute acids or alkalis. The *sodium salt* is a straw-yellow powder, readily soluble in water or alcohol. *Quinoline-6-stibinic chloride hydrochloride*, $C_9H_7NCl_5Sb$, is a buff microcrystalline powder, M.pt. 237° C.

Quinoline-8-stibinic acid,



occurs in two forms, (*a*) water-insoluble, (*b*) water-soluble. The former is prepared in the usual way and the following formula is assigned to it, $C_9H_6O_2NSb.\frac{2}{3}H_2O$. The water-soluble form is prepared by dissolving ordinary purified quinoline-8-stibinic acid in 0·2*N* acetic acid and evaporating the solution to dryness in a vacuum desiccator. The residue is redissolved in water, and the solution again evaporated to dryness *in vacuo*. The resulting light brown powder is readily soluble in water, the addition of a drop of sodium hydroxide resulting in the precipitation of the insoluble form. The formula of this compound by analysis is $C_9H_6O_2NSb.H_2O$. When concentrated hydrochloric acid is added to an ice-cold methyl alcoholic solution of the stibinic acid, small brownish needles of *quinoline-8-stibinic chloride hydrochloride* result. These decompose at 200° to 210° C. and have the constitution



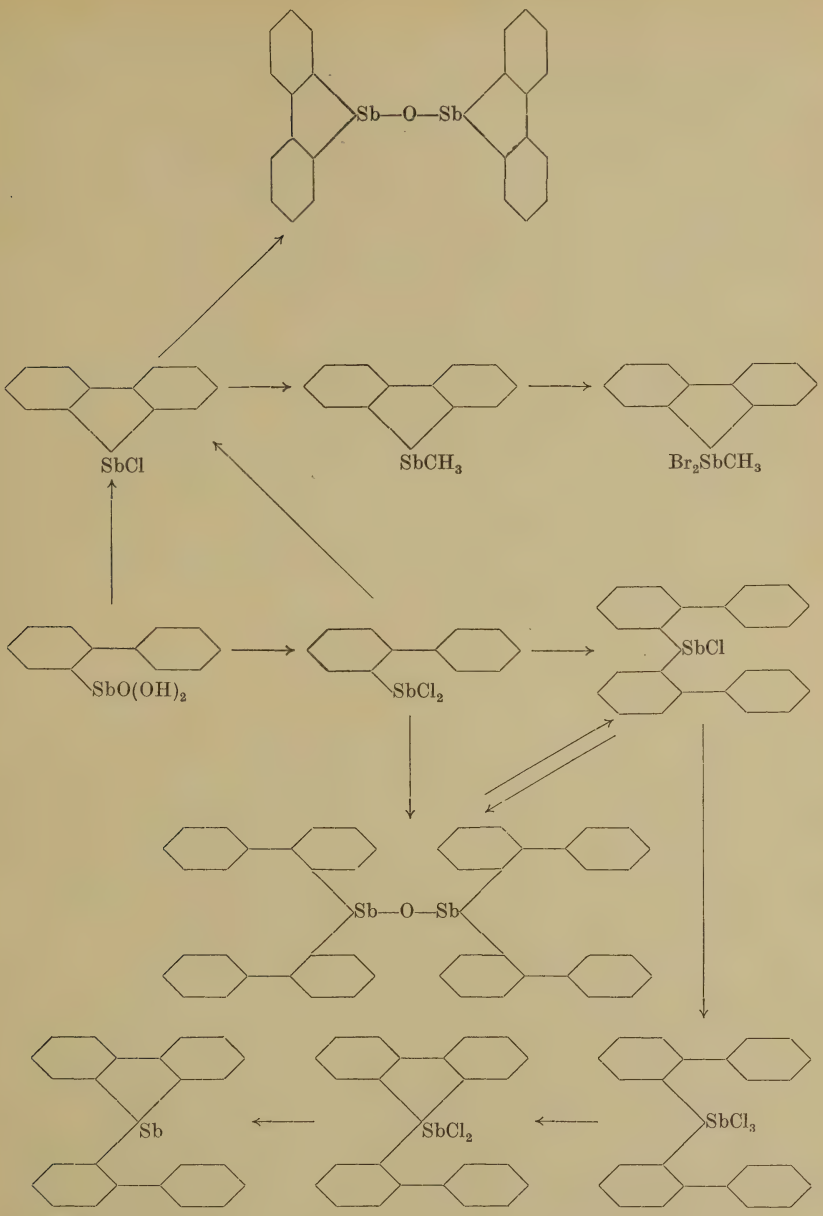
Antimonial Analogues of the Carbazole Series.[1]

The scheme on the next page indicates the compounds dealt with in this section.

It should be noted in connection with the nomenclature of these compounds that the term " xenyl " is employed for diphenylyl and " xenylene " for the bivalent radical of diphenyl.

Xenyl-o-stibinic acid, $C_6H_5.C_6H_4.SbO(OH)_2$.—*o*-Aminodiphenyl, 50 grams, in 300 c.c. of water and 160 c.c. of hydrochloric acid (density 1·16) is diazotised with 22 grams of sodium nitrite in 100 c.c. of water and to the diazo-solution are added 46 grams of antimony trioxide in 200 c.c. of hydrochloric acid (density 1·126), the temperature being maintained between 0° C. and 25° C. Diphenyl-*o*-diazonium antimony tetrachloride separates as a light yellow precipitate, and after washing

[1] Morgan and Davies, *Proc. Roy. Soc.*, 1930, A, **127**, 1.



with water this is suspended in 1500 c.c. of water containing 300 grams of ice, the mixture being cooled to 0° C.; 160 to 200 c.c. of glycerin are added and 5*N* sodium hydroxide slowly introduced with stirring until the mixture is faintly acid, about 300 c.c. of alkali being required. When frothing ceases, a further 30 c.c. of 5*N* sodium hydroxide are added and the liquid stirred until a sample no longer gives an azo-coloration with H-acid. The filtered liquid is acidified with dilute

hydrochloric acid and warmed to complete the precipitation of the stibinic acid, which is freed from inorganic antimony compounds by repeated washing with hydrochloric acid (density 1·126). The residue is extracted with 2·5*N* sodium hydroxide solution, the extract filtered and the filtrate acidified with acetic acid. The precipitated stibinic acid dries to a white amorphous powder, sparingly soluble in hot water, but separating from boiling alcohol as small, colourless crystals. Warm concentrated hydrochloric acid converts the acid into *xenyl-o-stibine tetrachloride*, $C_6H_5.C_6H_4.SbCl_4$, a yellow oil which yields *xenyl-o-stibine ammonium pentachloride*, $[C_6H_5.C_6H_4.SbCl_5]NH_4$, when shaken with a saturated solution of ammonium chloride in hydrochloric acid (density 1·126).

Xenyl-o-dichlorostibine, $C_6H_5.C_6H_4.SbCl_2$, occurs when a methyl alcohol hydrochloric acid solution of the foregoing acid containing a trace of potassium iodide is reduced by sulphur dioxide. The resulting mixture is extracted with chloroform and the oil obtained from the extraction is dissolved in ether and diluted with petroleum (B.pt. 60° to 80° C.), when rosettes of colourless needles separate on spontaneous evaporation, M.pt. 76° C. The product is very soluble in ordinary organic solvents. The dichloride is converted by sodium iodide in acetone solution to *xenyl-o-di-iodostibine*, $C_6H_5.C_6H_4.SbI_2$, which separates from alcohol as dark yellow needles, M.pt. 95° to 96° C.

Xenylenechlorostibine,

is obtained by heating xenyl-*o*-dichlorostibine at 100° C. under 25 mm. pressure, or as follows : 4 grams of xenyl-*o*-stibinic acid are added to 10 c.c. of cold concentrated sulphuric acid, to which 5 c.c. of the same acid are subsequently added. After warming on the water-bath for ten minutes the whole is poured into a large volume of water. The greyish-white precipitate which forms is washed, dried, and dissolved in warm hydrochloric acid with the minimum quantity of methyl alcohol. A fragment of potassium iodide is added and sulphur dioxide passed in until crystals appear. Excess of sulphur dioxide should be avoided and the temperature kept down, otherwise the antimony is entirely eliminated and diphenyl results. The crystals which deposit on standing are recrystallised from alcohol containing animal charcoal. The chloride separates as greenish-white acicular crystals, M.pt. 209° C., moderately soluble in hot chloroform, alcohol, acetone or benzene, less soluble in carbon disulphide or light petroleum. Sodium iodide in acetone converts the chloride into *xenyleneiodostibine*, lemon-yellow needles from benzene, M.pt. 222° C.

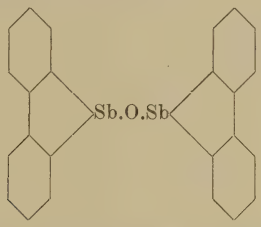
Xenylenemethylstibine, $(C_6H_4)_2Sb.CH_3$, is prepared by treating the preceding iodide with magnesium methyl iodide. It crystallises from petroleum as pale yellowish-white leaflets, M.pt. 57° C. It yields a *dibromide* as a pale yellow microcrystalline powder, M.pt. 207° C., slightly soluble in acetone or alcohol but not appreciably soluble in other organic solvents.

Tetrakis-o-xenylstibine oxide, $(C_6H_5.C_6H_4)_2Sb.O.Sb(C_6H_4.C_6H_5)_2$, is formed when crude xenyl-*o*-dichlorostibine is digested

with warm alkali, but preferably by adding an acetone solution of dixenyl-*o*-chlorostibine to a large volume of water containing sufficient ammonia to remain alkaline after heating the mixture on the water-bath. The oxide is washed with warm water, dissolved in hot acetone, and the solution rendered turbid by adding water. Evaporation of the solution yields large, colourless, flattened needles, M.pt. 157° C.

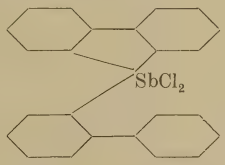
Dixenyl-o-chlorostibine, $(C_6H_5.C_6H_4)_2SbCl$.—Crude oily xenyl-*o*-dichlorostibine is poured into water and the liquid made slightly alkaline with sodium or ammonium hydroxide. The mixture is then warmed on the water-bath and the precipitate which forms dissolved in hot alcoholic hydrochloric acid, the chloride separating in colourless needles on cooling, M.pt. 125·5° C. It dissolves in most organic solvents, except light petroleum. The corresponding *iodide* may be obtained by the action of hydriodic acid on the foregoing oxide or sodium iodide in acetone on the chloride. It separates from alcohol or chloroform as light yellow prisms, M.pt. 156° to 157° C. Chlorine converts the chloride into the *trichloride*, small colourless needles, M.pt. 177° C.

Bis-2 : 2′-xenylenestibine oxide,



When an acetone solution of xenylenechlorostibine is poured into water containing a slight excess of ammonia, a white flocculent precipitate of this oxide separates. It crystallises from alcohol as yellowish-white spangles, M.pt. 177° to 179° C., readily soluble in chloroform, less soluble in alcohol, acetone or benzene, and insoluble in water or 2*N* sodium hydroxide.

Xenylene-o-xenyldichlorostibine,



When the foregoing trichloride is heated to 50° C. above its melting-point under 20 mm. pressure, hydrogen chloride is evolved; after cooling, the residual product is extracted with warm chloroform. After removing the solvent the solid is crystallised from chloroform-alcohol containing animal charcoal. Small white nodules separate, M.pt. 212° C., moderately soluble in organic solvents, except chloroform.

2 : 2′-Xenylene-o-xenylstibine,

occurs when the preceding chloride is suspended in 20 parts of alcohol and boiled for two hours with two parts of zinc dust. On filtering the concentrated solution large rosettes of colourless needles separate, M.pt. 106° to 107° C., readily soluble in organic solvents.

Water-soluble Organic Stibinous Compounds.

The derivatives here mentioned have the antimony atom bound to at least one carbon atom of an organic radical (preferably phenyl) and the remaining bond or bonds of the antimony joined to a sulphur atom or atoms, each sulphur atom being attached to the carbon of an organic radical containing an acid group, which has a free valency bond capable of being attached to hydrogen or a metal.[1]

p-Hydroxyphenyldichlorostibine reacts with two molecular proportions of *p*-mercaptobenzenesulphonic acid, yielding *p-hydroxyphenylstibinous p-thiobenzenesulphonic acid*, a white product which does not melt or decompose below 300° C., and yields a *sodium salt*. A similar product results with thioglycollic acid. *p*-Hydroxyphenyldi-iodostibine with thiosalicylic acid gives *p-hydroxyphenylstibinous thiosalicylic acid*, insoluble in water or ether, somewhat soluble in acetone or absolute alcohol, having an indefinite melting-point, decomposing when heated, and forming salts with *sodium*, *potassium*, *calcium* and like metals, also with *ammonium*. Similarly, *p-acetylaminophenylstibinous thiosalicylic* and *thiopropionic acids* are known, melting at about 200° and 105° to 107° C. respectively. Phenyldi-iodostibine gives *phenylstibinous thiobenzenesulphonic acid*, unmelted below 300° C., whilst the iodide, chloride or oxide may be converted into *phenylstibinous thiosalicylic acid*, M.pt. 186° C. *p-Acetylaminophenylstibinous thiobenzenesulphonic acid*, *p-aminophenylstibinous thiobenzenesulphonic acid*, *p-aminophenylstibinous thiosalicylic acid hydrochloride*, the corresponding *meta*-compound, and cysteine hydrochloride, give a white, hygroscopic product with *p*-acetylaminophenylstibinous chloride hydrochloride.

The Estimation of Antimony in Organic Compounds.

Schmidt's Process.—The following procedure is due to Schmidt :[2] Mono- and diaryl- stibine oxides, also triarylstibines, containing an amino-group substituted in the benzene nucleus, can be estimated directly by titration with iodine in very dilute and faintly acid solution. A more general process consists of heating to boiling about 0·001 of a molecular proportion of the substance, 0·2 gram of sodium chloride and 3 grams of sodium bisulphate mixed in a Kjeldahl flask with 1·5 c.c. of nitric acid (density 1·49) and 10 c.c. of concentrated sulphuric acid, the heating being maintained for an hour. After cooling, a gram of ammonium sulphate is added and the whole again boiled for thirty minutes. The mixture is then diluted to about 300 c.c., and 20 c.c. of 5*N* hydrochloric acid added, followed by reduction by sulphur dioxide in the presence of potassium bromide. The solution is finally titrated with *N*/10 iodine solution made alkaline to sodium bicarbonate.

Macallum's Process.[3]—The substance, 0·2 gram, is dissolved if

[1] American Patent, 1684920.
[2] Schmidt, *Annalen*, 1920, 421, 244, 245.
[3] Macallum, *J. Soc. Chem. Ind.*, 1923, 49, 469 T.

possible in 10 c.c. of water by addition of alkali, and treated with one gram of potassium permanganate and 10 c.c. of concentrated sulphuric acid. After heating for a time the mixture is decolorised by boiling with 10 to 15 c.c. of hydrochloric acid and diluted with 50 c.c. of water and 75 c.c. of hydrochloric acid. The antimony is reduced in the cooled solution by shaking for three minutes with 5 grams of potassium iodide. After diluting with a further 125 c.c. of water, the solution is titrated with $N/10$ sodium thiosulphate solution, using starch as indicator. If a blank be subtracted, each cubic centimetre of thiosulphate solution is equivalent to 0·006 gram of antimony, or 3 per cent. The quinquevalent antimony in a preparation may usually be titrated directly under the foregoing conditions, omitting, of course, the permanganate and sulphuric acid.[1]

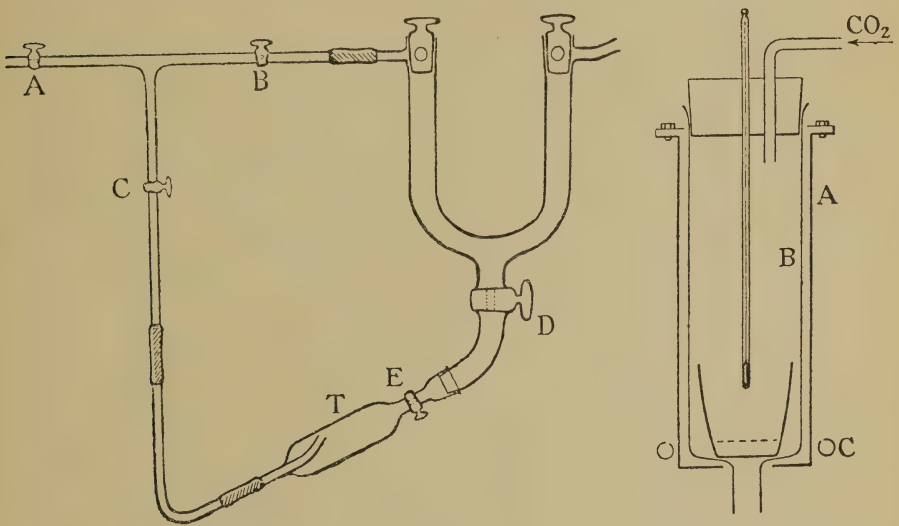


Fig. 6.

For readily oxidised antimony compounds the following method and apparatus is used, taking as an example dimethylstibine bromide.[2]

Owing to the difficulty of weighing out the dimethylstibine bromide without oxidation taking place, the apparatus shown in the figure was designed for the analysis of easily oxidised or spontaneously inflammable liquids.

The apparatus having been filled with nitrogen, the stop-cocks A and B are opened, and C, D and E kept closed, the stop-cocks at the top of the U-tube also being open. A vacuum of about 60 mm. is used and the dimethylstibine bromide or other antimonial distilled into the U-tube. The vacuum is then released with nitrogen, and enough

[1] The following are further references to antimony estimation: Michaelis and Reese, *Annalen*, 1886, **233**, 46; Michaelis and Genzken, *Annalen*, 1887, **242**, 168; Löloff, *Ber.*, 1897, **30**, 2835; Rohmer, *Ber.*, 1901, **34**, 1565; Cahen and Morgan, *Analyst*, 1909, **34**, 3; Fargher and Gray, *J. Pharm. and Exper. Therap.*, 1921, **18**, 356.

The following deals with the estimation of antimony in the presence of arsenic: Schmidt, *Ber.*, 1924, **57**. [B], 1148.

[2] Morgan and Davies, *Proc. Roy. Soc.*, 1926, A, **110**, 523.

of the bromide for a combustion run into T, the taps C, D and E being open. The tap D having been closed, the small tube T is taken out, stoppers placed on both ends, and weighed. The weight of the empty tube has previously been ascertained. The stoppers are then quickly removed, the tap E opened, and the tube, after being wrapped in a little asbestos paper, is placed in an 18 mm. combustion tube.

Liquid antimonials have hitherto been oxidised with nitric acid and the antimony estimated as Sb_2O_4. Some of them, however, react too vigorously with nitric acid to permit of this method being used with success. Moreover, the process involves very careful control of the temperature to which the Sb_2O_5—Sb_2O_4 mixture is heated in order to obtain only Sb_2O_4. Consequently, the following method has been evolved and found to give very consistent results :

The required amount of antimonial is weighed out and heated in a 250 c.c. beaker with 15 to 20 c.c. of concentrated sulphuric acid and 1 to 2 c.c. of nitric acid (density 1·42). The amount of nitric acid required varies with the percentage of carbon present in the compound to be analysed. The mixture is heated until 4 to 5 c.c. of the sulphuric acid remain. When cool, the liquid is diluted to 50 c.c. and 20 c.c. of concentrated hydrochloric acid are added, together with 50 c.c. of phosphoric acid (density 1·3). The solution is then treated with sulphuretted hydrogen at 100° C. until black antimony sulphide is obtained, 60 to 70 c.c. of water are added, and the gas passed in until the crystalline antimony sulphide is completely precipitated. The sulphide is filtered into a Gooch crucible, washed with sulphuretted hydrogen, and dried in the following manner : The crucible is placed in the glass tube B shown in the figure, which is fitted into a copper cylinder A. This cylinder is 20 cm. long, has an internal diameter of 3·7 cm., and is lined on the inside with thin asbestos paper. Carbon dioxide is passed in, and by means of the ring burner C the crucible is heated slowly to 120° C. for about half an hour, and then raised to 280° C., being kept at this temperature for $1\frac{1}{2}$ to 2 hours.

For the estimation of antimony in trialkylstibines the following method has been used : [1] The compound is heated with sodium carbonate in a stream of oxygen in a combustion tube. The contents of the tube are then dissolved in 10 per cent. hydrochloric acid and antimony trisulphide precipitated from the boiling solution by passing in hydrogen sulphide for 30 minutes. An equal volume of hot water is then added to the liquid and the stream of hydrogen sulphide continued for five minutes. The precipitate is collected on a Gooch crucible, washed, dried for two hours at 130° C., then heated for two hours at 280° to 300° C. in a carbon dioxide atmosphere and weighed.

[1] Dyke, Davies and Jones, *J. Chem. Soc.*, 1930, p. 463.

CHAPTER VI.

ORGANOMETALLIC DERIVATIVES OF BISMUTH.

The element bismuth does not tend to form organometallic derivatives with the same facility as the other members of Group V. In the case of phosphorus pentavalent compounds of the type R_3PX_2 are unknown in the aromatic series, whereas these are the most stable derivatives in the case of bismuth. It is more than forty years since any systematic research on aliphatic bismuth compounds was carried out, so that, whilst giving the data found in the literature, the author would not care to vouch for the correctness of some of the work described in the light of more modern work on the aromatic series. The aliphatic bismuthines fall into three classes, R_3Bi, R_2BiX and $RBiX_2$, where X is a monovalent element or radical.

The chief methods of preparing aliphatic compounds of the type R_3Bi are as follows:—

(1) Zinc dialkyls in dry ether solution are allowed to react with bismuth halides:

$$3ZnR_2 + 2BiX_3 = 2R_3Bi + 3ZnX_2$$

(2) Alloys of bismuth and potassium are treated with alkyl iodides:

$$K_3Bi + 3RI = R_3Bi + 3KI$$

The trialkylbismuthines are highly refractive liquids which fume in air and have a tendency to explode when heated. Concentrated sulphuric acid causes violent decomposition, concentrated hydrochloric acid acting with less vigour but with a similar result. Treatment with chlorine or bromine eliminates an alkyl radical forming compounds of the type R_2BiX, and with trimethylbismuthine, methyl iodide at 200° C. yields methyldi-iodobismuthine. Mercuric chloride converts triethylbismuthine into ethyldichlorobismuthine, whilst hydrogen sulphide breaks it down to bismuth sulphide.

The second class of compounds, namely R_2BiX, although represented by solid products, is a decidedly unstable class. The compounds are prepared by the halogenation of the tertiary bismuthines:

$$R_3Bi + X_2 = R_2BiX + RX$$

The remaining type, $RBiX_2$, occurs when the trialkylbismuthines are treated with bismuth halides or mercuric halides:

$$R_3Bi + 2BiX_3 = 3RBiX_2$$
$$R_3Bi + 2HgX_2 = 2RHgX + RBiX_2$$

In the case of methyldi-iodobismuthine or ethyldi-iodobismuthine their preparation has also been effected by the action of methyl or ethyl

iodide on the tertiary bismuthine at high temperatures or, in the latter case, by treating ethyldichlorobismuthine with potassium iodide. Silver nitrate replaces the two halogen atoms of ethyldi-iodobismuthine by two nitrate radicals.

Far more information is available in connection with aromatic bismuthines. The methods available for the preparation of compounds of the type R_3Bi are as follows :—

(1) Heating together an aryl bromide and sodium-bismuth alloy for a long period. This method gives yields as high as 75 per cent. :

$$Na_3Bi + 3RBr = R_3Bi + 3NaBr$$

(2) The interaction of aryl magnesium halides and bismuth halides, the yield being about 60 per cent. :

$$3MgRX + BiX_3 = R_3Bi + 3MgX_2$$

(3) Mixing dry ether solutions of mercury diphenyl and bismuth bromide gives quantitative yields of triphenylbismuthine. This method is undoubtedly applicable to other aromatic bismuthines, the obvious drawback being the preparation of the mercury diaryls, which would involve as much difficulty as using methods (1) or (2) above :

$$3R_2Hg + 2BiX_3 = 2R_3Bi + 3HgX_2$$

(4) Heating mercury diphenyl with metallic bismuth in a stream of hydrogen for ten minutes, the yield being 41 per cent. :

$$3R_2Hg + 2Bi = 2R_3Bi + 3Hg$$

(5) The removal of the halogen from triarylbismuthine dihalides by means of sodium hydrosulphite, aqueous or alcoholic alkali, or moist silver oxide.

Only one mixed tertiary bismuthine is known, namely, diphenyl-α-naphthylbismuthine. It may be obtained by the interaction of triphenylbismuthine and tri-α-naphthylbismuthine, or by the following Grignard reactions :—

$$(C_6H_5)_2BiBr + C_{10}H_7MgBr = (C_6H_5)_2(C_{10}H_7)Bi + MgBr_2$$
$$C_{10}H_7BiBr_2 + 2C_6H_5MgBr = (C_6H_5)_2(C_{10}H_7)Bi + 2MgBr_2$$

The reactions of various substances with triphenylbismuthine are shown in the table on opposite page, and are typical for the type R_3Bi.

Aryldihalogenobismuthines are few in number and tend to be unstable, especially in the presence of moisture. They are formed

(1) When triarylbismuthines are treated with bismuth halides :

$$R_3Bi + BiX_3 = R_2BiX + RBiX_2$$
$$2R_2BiX = RBiX_2 + R_3Bi$$

(2) By the addition of halogens to diarylhalogenobismuthines :

$$R_2BiX + X_2 = RBiX_2 + RX$$

(3) By the decomposition of dry triarylbismuthine dihalides by heat. All the products in this class are solids.

The compounds of the type R_2BiX share the property of instability possessed by the $RBiX_2$ derivatives. They occur along with com-

REACTIONS OF TRIPHENYLBISMUTHINE.

Reacting Substance.	Resulting Products.	References.
Chlorine or bromine.	Triphenylbismuthine dichloride or dibromide.	Michaelis and Marquardt, *Annalen*, 1889, **251**, 323.
Iodine.	Diphenyliodobismuthine and iodobenzene.	Gillmeister, *Ber.*, 1897, **30**, 2843; Challenger and Allpress, *Trans. Chem. Soc.*, 1915, **107**, 16.
Iodine monochloride or monobromide.	Diphenylchlorobismuthine or diphenylbromobismuthine and iodobenzene.	Challenger and Allpress, *ibid.*
Cyanogen iodide.	Diphenylcyanobismuthine and iodobenzene.	do.
Thiocyanogen.	Diphenylthiocyanobismuthine, bismuth thiocyanate, polymerised thiocyanogen and phenyl thiocyanate.	Challenger and Wilkinson, *Trans. Chem. Soc.*, 1922, **121**, 91.
Thiocyanic acid.	Diphenylthiocyanobismuthine.	Challenger, Smith and Paton, *ibid.*, 1923, **123**, 1054.
Acetyl chloride or benzoyl chloride.	Diphenylchlorobismuthine and aceto- or benzo- phenone.	Challenger and Ridgway, *ibid.*, 1922, **121**, 104.
Phosphorus trichloride.	Diphenylchlorobismuthine and phenyldichlorophosphine.	do.
Arsenic trichloride.	Diphenylchlorobismuthine, phenyldichloroarsine and diphenylchloroarsine.	do.
Antimony trichloride.	Diphenylchlorobismuthine and triphenylstibine dichloride.	do.
Bismuth trichloride.	Diphenylchlorobismuthine.	do.
Bismuth tribromide.	Phenyldibromobismuthine.	Challenger and Allpress, *ibid.*, 1921, **119**, 919.
Mercuric chloride.	Diphenylchlorobismuthine and phenylmercuric chloride.	Challenger and Ridgway, *loc. cit.*
Silver nitrate.	Compound $AgNO_3.2AgC_6H_5$?	do.
Cupric chloride.	Diphenylchlorobismuthine and cuprous chloride.	do.
Thallic chloride.	Diphenylchlorobismuthine and thallium diphenyl chloride.	Goddard, *ibid.*, 1922, **121**, 36.
Stannic chloride.	Tin diphenyl hydroxychloride and tin diphenyl dichloride.	Challenger and Pritchard, *ibid.*, 1924, **125**, 864.
Silicon tetrachloride.	Diphenylchlorobismuthine.	do.
Titanium tetrachloride.	do.	do.

pounds of the type $RBiX_2$ when bismuth halides react with triarylbismuthines. The iodo-compounds are formed also by treating the type R_3Bi with iodine. Iodine monochloride or cyanogen iodide also removes an aryl group from triarylbismuthines:

$$R_3Bi + ICl = R_2BiCl + RI$$
$$R_3Bi + CNI = R_2BiCN + RI$$

Bismuth halides interact with lead tetra-aryls to yield similar products:

$$R_4Pb + BiX_3 = R_2BiX + R_2PbX_2$$

Certain triarylbismuthine dibromides when boiled in dry benzene eliminate aryl bromide:

$$R_3BiBr_2 = R_2BiBr + RBr$$

The halogen may be removed from triarylbismuthine dihalides by salts such as potassium cyanide or lead thiocyanate:

$$R_3BiX_2 + KCN = R_2BiCN + KX + RX$$
$$R_3BiX_2 + Pb(CNS)_2 = R_2BiCNS + PbX_2 + RCNS$$

The pentavalent bismuth derivatives, R_3BiX_2, form a relatively stable class of compounds. The most important members are the dichlorides, R_3BiCl_2, and the dibromides, R_3BiBr_2, since from these substances most of the other compounds in the class may be derived. Chlorine and bromine add on directly to triarylbismuthines in dry solvents:

$$R_3Bi + Cl_2(\text{or } Br_2) = R_3BiCl_2(\text{or } Br_2)$$

These two halogens may be replaced by other elements or radicals by treatment with such inorganic salts as potassium fluoride or silver salts:

$$R_3BiCl_2 + 2KF = R_3BiF_2 + 2KCl$$
$$R_3BiCl_2 + 2AgNO_3 = R_3Bi(NO_3)_2 + 2AgCl$$

Solution in concentrated sulphuric acid produces sulphates, with elimination of halogen acid:

$$R_3BiCl_2 + H_2SO_4 = R_3BiSO_4 + 2HCl$$

Treatment with sodium hydroxide, followed by carbon dioxide, yields carbonates:

$$R_3BiBr_2 \longrightarrow [R_3Bi(OH)_2] \longrightarrow R_3BiCO_3$$

The carbonates dissolve in acids to yield other salts; in the case of acetic acid the diacetate is formed. The latter also occurs when an acetic acid solution of a triarylbismuthine dihalide is heated with lead acetate. Moist ammonia converts the dihalides to hydroxyhalides, $R_3Bi(OH)X$. It is noteworthy that no di-iodides have been isolated, iodine always causing the elimination of aryl groups. Certain of the dihalides have been nitrated, but the investigation is as yet not sufficiently advanced to call for special comment regarding the position of the nitro-groups. The following table shows the typical reactions of the type R_3BiX_2.

REACTIONS OF BISMUTHINE DERIVATIVES OF THE TYPE R_3BiX_2.

Bismuthine.	Reacting Substance.	Resulting Products.	References.
Triphenylbismuthine dichloride or dibromide.	Moist silver oxide or aqueous or alcoholic potassium hydroxide.	Triphenylbismuthine and silver halide or potassium halide.	Challenger and Goddard, *Trans. Chem. Soc.*, 1920, 117, 762.
Triphenylbismuthine dichloride.	Concentrated sulphuric acid.	Triphenylbismuthine sulphate and hydrogen chloride.	do.
do.	Moist ammonia.	Triphenylbismuthine hydroxychloride.	do.
do.	*p*-Tolyl magnesium bromide.	Triphenylbismuthine.	do.
Triphenylbismuthine hydroxychloride.	Methyl magnesium iodide.	Triphenylbismuthine dichloride and triphenylbismuthine.	do.
Triphenylbismuthine difluoride.	Phenyl magnesium bromide.	Triphenylbismuthine and fluorobenzene.	Challenger and Wilkinson, *ibid.*, 1922, 121, 91.
Triphenylbismuthine dichloride.	Potassium hydrogen fluoride.	Triphenylbismuthine.	do.
do.	Potassium cyanide.	Diphenylcyanobismuthine.	do.
do.	Lead thiocyanate.	Diphenylthiocyanobismuthine.	do.
Tri-α-naphthylbismuthine dichloride.	Moist silver oxide.	Tri-α-naphthylbismuthine and silver chloride.	Challenger and Goddard, *loc. cit.*
do.	Potassium cyanide.	Tri-α-naphthylbismuthine and potassium chloride.	Challenger and Wilkinson, *loc. cit.*
do.	Potassium thiocyanate.	Tri-α-naphthylbismuthine, bismuth oxychloride, and potassium chloride.	do.
do.	Lead thiocyanate.	Tri-α-naphthylbismuthine, α-naphthyl thiocyanate and lead chloride.	do.
Tri-α-naphthylbismuthine dibromide	Mercury diphenyl.	Tri-α-naphthylbismuthine, diphenyl-α-naphthylbismuthine, mercury di-α-naphthyl, phenylmercuric bromide and bromobenzene.	Challenger and Allpress, *ibid.*, 1921, 119, 913.

Aliphatic Compounds of the Type R_3Bi.

Trimethylbismuthine, $(CH_3)_3Bi$.—This compound may be isolated [1] by the interaction of bismuth bromide and zinc dimethyl in dry ether solution. The ether is distilled off in a carbon dioxide atmosphere, and after treatment of the residue with caustic soda, the bismuthine is distilled off in a current of hydrogen.

A more recent method of preparation [2] is as follows : 50 grams of crystalline bismuth trichloride are dissolved in 150 grams of 20 per cent. hydrochloric acid and shaken in a stream of carbon dioxide with 60 grams of aluminium carbide, which is slowly added in portions of 5 grams. The reaction takes about three hours to complete, after which the product is extracted three times with 200 c.c. of ether in an atmosphere of carbon dioxide or hydrogen, the ether then being removed *in vacuo* at 10° C. A yield of about 20 grams of trimethylbismuthine results from the foregoing quantities.

Trimethylbismuthine is a transparent, highly refractive liquid, distilling in an indifferent gas stream at about 110° C., but exploding violently on heating in air. It fumes in air, and the vapours attack the mucous membranes. It is readily oxidised. It has a density of 2·30 at 18° C. It is easily soluble in ether, alcohol, acetic acid or petroleum ether, insoluble in water, but decomposed on long boiling with the latter; it is volatile in steam. Contact with concentrated sulphuric acid causes explosion, but concentrated hydrochloric acid reacts as follows :—

$$(CH_3)_3Bi + 3HCl = BiCl_3 + 3CH_4$$

Treatment with chlorine or bromine yields compounds of the type $R_2BiHal.$, and the type $RBiHal._2$ is produced by the action of bismuth chloride or bromide or mercuric halides. It does not react with methyl iodide at 150° C., but at about 200° C. ethane and methyl di-iodobismuthine are produced.

Triethylbismuthine, $(C_2H_5)_3Bi$, has been obtained by the action of ethyl iodide on potassium-bismuth alloy,[3] and from bismuth bromide and zinc diethyl. It is a fuming oil, distilling unchanged at 107° C. at 79 mm., and exploding when heated in air at ordinary pressures.[4] Its density is 1·82. Its solubility and behaviour towards halogens is similar to that of the methyl compound. Evaporation of its ether solution in the presence of air leads to the formation of bismuth hydroxide, and if the solution be saturated with hydrogen sulphide, bismuth sulphide separates. If to a warm dilute alcoholic solution of triethylbismuthine a similar solution of mercuric chloride is added, a precipitate of mercurous chloride is thrown down ; but if the order of addition is reversed, ethylmercuric chloride and ethyldichlorobismuthine are produced :

$$(C_2H_5)_3Bi + 2HgCl_2 = 2C_2H_5HgCl + C_2H_5BiCl_2$$

Triethylbismuthine sulphide, $(C_2H_5)_3BiS$.—It has been stated that an ether solution of triethylbismuthine, when saturated with hydrogen sulphide, yields bismuth sulphide. When the latter is filtered off and the mother liquor treated with water, a yellow powder is

[1] Marquardt, *Ber.*, 1887, **20**, 1516.
[2] Hilpert and Ditmar, *Ber.*, 1913, **46**, 3738.
[3] Breed, *Annalen*, 1852, **82**, 106.
[4] Dünhaupt, *Annalen*, 1854, **92**, 371.

formed, insoluble in water but easily soluble in ammonium sulphide. This approximates to the composition $(C_2H_5)_3BiS.Bi_2S_3$.

Tri-isobutylbismuthine,[1] $(C_4H_9)_3Bi$, is prepared in a similar way to the methyl derivative, from zinc di-*iso*butyl and bismuth bromide, the reaction mixture being treated with sodium hydroxide, when the bismuthine separates out as an oil. It is a colourless liquid, B.pt. 160° to 162° C. at 74 mm., having a faint odour, fuming in air and burning with a dull yellow flame. Even when distilled under reduced pressure it partially decomposes, with separation of metallic bismuth.

Tri-isoamylbismuthine, $(C_5H_{11})_3Bi$, has similar properties to the foregoing compound, and distils in a carbon dioxide atmosphere at 190° to 200° C. at 70 mm.

Aliphatic Compounds of the Type R_2BiX.

Dimethylchlorobismuthine,[2] $(CH_3)_2BiCl$.—When trimethylbismuthine in petroleum ether is chlorinated, the solution being well cooled, the monochloro-compound separates out as a white microcrystalline powder, which melts at 116° C. in a sealed tube. It is easily soluble in alcohol, but not in ether, and cannot be recrystallised without decomposition.

Dimethylbromobismuthine, $(CH_3)_2BiBr$, is obtained in a similar manner to the chloro-compound, the operation being carried out in a carbon dioxide atmosphere. It resembles the chloride in properties.

Dimethylhydroxybismuthine, $(CH_3)_2BiOH$.—When trimethylbismuthine (2 mols.) and bismuth bromide (1 mol.) are allowed to react in ether solution, an oil is produced, which yields the hydroxide when treated with water. The compound is not stable when dry, and with hydrochloric acid it reacts as follows:—

$$(CH_3)_2BiOH + 3HCl = 2CH_4 + BiCl_3 + H_2O$$

When heated with methyl iodide at 100° C., methyldi-iodobismuthine is formed, and with ammonium hydroxide or alcohol bismuth hydroxide is precipitated.

Diethylbromobismuthine, $(C_2H_5)_2BiBr$, is prepared in a similar manner to the methyl compound, and is a white powder, igniting in air, with the formation of bismuth oxide.

Di-isobutylbromobismuthine,[3] $(C_4H_9)_2BiBr$, is obtained by bromination of the tertiary bismuthine in a carbon dioxide atmosphere. It forms white crystalline tablets, which are easily soluble in alcohol, but soluble with difficulty in ether or petroleum. On exposure to the air or on heating it burns with formation of bismuth oxide.

Di-isoamylbromobismuthine, $(C_5H_{11})_2BiBr$, has not been isolated in a pure state, the product obtained forming white crystals, easily soluble in alcohol, but soluble with difficulty in ether.

Aliphatic Compounds of the Type $RBiX_2$.

Methyldichlorobismuthine, $CH_3.BiCl_2$.[4]—This compound is formed according to the equation:

$$(CH_3)_3Bi + 2BiCl_3 = 3CH_3.BiCl_2$$

[1] Marquardt, *Ber.*, 1888, **21**, 2035.
[2] Marquardt, *Ber.*, 1887, **20**, 1516.
[3] Marquardt, *Ber.*, 1888, **21**, 2035.
[4] Marquardt, *Ber.*, 1887, **20**, 1516.

To a solution of bismuth chloride in acetic acid the calculated quantity of trimethylbismuthine is added, the methyldichlorobismuthine separating out as yellowish-white plates, M.pt. 242° C. These are somewhat soluble in alcohol or acetic acid, but insoluble in ether.

Methyldibromobismuthine, $CH_3.BiBr_2$, is prepared in the same way as the preceding compound, using bismuth bromide. It is a yellow powder, M.pt. 214° C., soluble with difficulty in alcohol, acetic acid or benzene, and insoluble in ether.

Methyldi-iodobismuthine, $CH_3.BiI_2$, may be prepared by the usual method or by the interaction of trimethylbismuthine and methyl iodide at 200° C. It forms brick-red crystals, melting without decomposition at 225° C., somewhat soluble in alcohol, soluble with difficulty in hot acetic acid, and insoluble in ether.

Methylbismuthine oxide, $CH_3.BiO$.—Two molecular equivalents of trimethylbismuthine in ether solution are treated with four equivalents of bismuth bromide, and the precipitate obtained, after washing with ether, is dissolved in alcohol. Addition of ammonium hydroxide to the solution precipitates the oxide, which is insoluble in water and soluble with difficulty in ammonia, but dissolves in dilute hydrochloric acid. It soon decomposes on warming or standing in the air.

Ethyldichlorobismuthine, $C_2H_5.BiCl_2$, may be prepared in a similar manner to the methyl compound, or by the action of mercuric chloride on alcoholic triethylbismuthine. It crystallises in plates, which yield ethyldi-iodobismuthine when treated with potassium iodide.

Ethyldi-iodobismuthine,[1] $C_2H_5.BiI_2$, may be prepared (1) by the action of aqueous potassium iodide on ethyldichlorobismuthine, (2) by treating triethylbismuthine with ethyl iodide at a high temperature. It forms seven-sided golden-yellow plates, which are easily soluble in alcohol, soluble with difficulty in ether, and very slightly soluble in water. When an aqueous alcohol solution of the compound is treated with a slight excess of sodium hydroxide, a yellowish-white precipitate appears, which is not stable in the air when dry, and is probably *ethylbismuthine oxide*, since it forms salts with acids. The alcoholic di-iodobismuthine solution, treated with hydrogen sulphide, deposits bismuth sulphide, and with silver sulphate the organic bismuth sulphate, presumably formed, decomposes when the solution is concentrated.

Ethylbismuthine dinitrate, $C_2H_5.Bi(NO_3)_2$.—When the foregoing di-iodo-compound is treated with alcoholic silver nitrate, the silver iodide filtered off and the filtrate concentrated, the cooled liquid solidifies to a crystalline mass, which on gentle warming explodes. Analysis shows the crystals to be the dinitrate.

isoButyldibromobismuthine, $C_4H_9.BiBr_2$, prepared from tri-*iso*butylbismuthine and bismuth bromide, crystallises in honey-yellow monoclinic prisms, which are readily soluble in alcohol or acetic acid, but soluble with difficulty in ether. It is unaffected by air, and melts at 124° C. When heated with methyl or ethyl iodide in a sealed tube at 150° C. the principal products appear to be trimethylbismuthine or triethylbismuthine, not *iso*butyldi-iodobismuthine, which is unknown.

isoAmyldibromobismuthine, $C_5H_{11}.BiBr_2$.—The product obtained melts at 134° C., but cannot be completely freed from bismuth bromide; the determination of the metal is therefore high.

[1] Compare Dünhaupt, *Annalen*, 1854, **92**, 371.

Aromatic Compounds of the Type R_3Bi.

Triphenylbismuthine,

may be obtained in a variety of ways : (1) By heating together equal weights of bromobenzene and sodium-bismuth alloy for a prolonged period. The yield is about 75 per cent.[1] (2) By the action of phenyl magnesium bromide on bismuth chloride or bromide.[2] To the solution from 11 grams of bromobenzene and 2·5 grams of magnesium in dry ether, 10 grams of anhydrous bismuth bromide are slowly added, the whole being cooled in water during the addition. The mixture is then heated for two hours on the water-bath, cooled and decomposed with water, the ether layer being separated off and dried. Distillation away of the solvent yields 6·5 grams (53 per cent.) of the crude bismuthine.[3] (3) When 3·5 grams of mercury diphenyl and 1·5 grams of bismuth bromide are mixed in dry ether, 1·6 grams of triphenylbismuthine are isolated, the yield being quantitative.[4] (4) By heating mercury diphenyl and metallic bismuth in a stream of hydrogen at 250° C. for ten minutes a 41 per cent. yield of the bismuthine is obtained.[5]

Triphenylbismuthine crystallises from ether or alcohol in colourless needles, M.pt. 78° C. Michaelis [6] states that it exists in two forms, melting at 75° C. and 78° C. respectively, but this observation has never been substantiated. When treated with chlorine or bromine in suitable solvents it yields triphenylbismuthine dichloride or dibromide respectively, but with iodine, only diphenyliodobismuthine is produced, the pentavalent derivative in this case appearing to be unstable. With concentrated hydrochloric acid the bismuthine is decomposed, yielding benzene and bismuth chloride, and this reaction appears to be a general one, which may be used for the detection of aromatic bismuthines. An ether solution of triphenylbismuthine, when treated with bismuth bromide, is degraded to phenyldibromobismuthine,[7] and with bismuth chloride the diphenylchloro-compound is produced.[8] When a benzene solution of triphenylbismuthine is refluxed with cyanogen iodide, diphenylcyanobismuthine is formed, and acetyl and benzoyl chlorides react with production of diphenylchlorobismuthine and acetophenone or benzophenone respectively, the operation being conducted in carbon tetrachloride.

Tri-p-chlorophenylbismuthine,[9]

[1] Michaelis and Polis, *Ber.*, 1887, 20, 52.

[2] Pfeiffer and Pietsch, *Ber.*, 1904, 37, 4620; compare Stilp, *Inaug. Dissert. Rostock*, 1910.

[3] A slightly better yield is obtained if, instead of decomposing the mixture after heating on the water-bath, the ether first be distilled off and the residue baked on the water-bath for a day before decomposing it.—Author.

[4] Challenger and Allpress, *Trans. Chem. Soc.*, 1921, 119, 913.

[5] Hilpert and Grüttner, *Ber.*, 1913, 46, 1675.

[6] Michaelis and Polis, *loc. cit.*

[7] Michaelis and Marquardt, *Annalen*, 1889, 251, 323.

[8] Challenger and Allpress, *Trans. Chem. Soc.*, 1915, 107, 16.

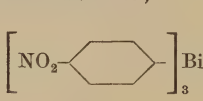
[9] Challenger and Ridgway, *Trans. Chem. Soc.*, 1922, 121, 104.

is prepared by treating the ether solution of magnesium *p*-chlorophenyl bromide from 50 grams of *p*-chlorobromobenzene, 6·3 grams of magnesium and 0·5 gram of iodine, with 24·6 grams of bismuth chloride in dry ether. When the reaction subsides the ether is removed and the mixture heated at 100° C. for four hours, then treated with water, phenyl halides or diphenyl derivatives being removed in steam, and the filtered residue extracted with acetone. The material deposited from the latter solvent on recrystallisation from ethyl acetate-acetone mixture melts at 116° C. The bismuthine is readily soluble in most organic solvents, but sparingly soluble in alcohol or light petroleum. With hydrochloric acid it yields chlorobenzene, and its behaviour towards the halogens is similar to that of triphenylbismuthine.

Tri-p-bromophenylbismuthine,

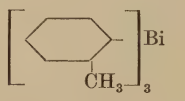
is isolated as a white, granular powder, by the interaction of magnesium *p*-bromophenyl bromide (3 mols.) and anhydrous bismuth bromide (1 mol.). It melts at 149° C. and has a similar solubility to the chloro-derivative.

Tri-p-nitrotriphenylbismuthine,[1]



A solution of 2 grams of tri-*p*-nitrophenylbismuthine dichloride in 10 c.c. of acetone is cooled to 0° C. and treated with 8 grams of sodium hydrosulphite. The yellow precipitate is removed at 0° C., washed thrice with water, dissolved in acetone and the solution allowed to evaporate spontaneously. The residue is heated to boiling in alcohol, the solution filtered and partly evaporated, a white powder resulting. Recrystallisation from acetone gives a product melting at about 121° C. The compound tends to decompose on standing.

Tri-o-tolylbismuthine,[2]

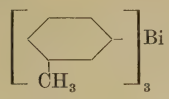


is obtained (1) by heating *o*-bromotoluene and sodium-bismuth alloy in the presence of ethyl acetate for a long time at 180° to 200° C., (2) from *o*-tolyl magnesium bromide and bismuth bromide. It forms rhombic crystals, M.pt. 128·5° C., soluble in ether, benzene, chloroform or ligroin, less soluble in alcohol. When its alcohol solution is treated with mercuric chloride in the same solvent, a *mercurichloride* is precipitated, $(C_7H_7)_3Bi.HgCl_2$. This separates from hot acetic acid as fine white needles, M.pt. 148° C.

[1] Supniewski, *Rocz. Chem.*, 1925, 5, 298; Supniewski and Adams, *J. Amer. Chem. Soc.*, 1926, 48, 507.

[2] Gillmeister, *Ber.*, 1897, 30, 2843; Stilp, *Inaug. Dissert. Rostock*, 1910.

Tri-m-tolylbismuthine,[1]

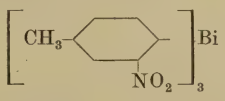


crystallises from acetone or alcohol in white needles, M.pt. 65° C.[2]

Tri-p-tolylbismuthine,[3]

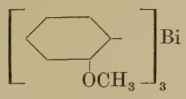
gives transparent prisms, M.pt. 119° to 120° C., easily soluble in benzene, chloroform or ligroin, sparingly soluble in alcohol. The yield, using the Grignard reaction for the preparation, is about 55 per cent. It forms a *mercurichloride*, which separates from hot acetic acid in glistening plates, M.pt. 234° C., readily soluble in chloroform, insoluble in alcohol or ether. The bismuthine reacts with thallic chloride to yield di-*p*-tolylchlorobismuthine and thallium di-*p*-tolyl chloride.[4]

Tri-2-nitrotri-p-tolylbismuthine,[5]



is a yellow compound formed in a similar manner to the phenyl derivative. When purified from ethyl acetate it melts at 126° C.

Tri-o-anisylbismuthine,[6]



isolated from *o*-anisyl magnesium bromide and bismuth bromide, using iodine as a catalyst, may be crystallised from chloroform or benzene. It is a white crystalline powder, M.pt. 168° to 170° C., easily soluble in benzene, sparingly soluble in alcohol or ether.

Tri-p-anisylbismuthine,[7]

may be obtained (1) by heating *p*-bromoanisole with sodium-bismuth alloy at 180° C., (2) from *p*-anisyl magnesium bromide and bismuth bromide, the product separating from alcohol-benzene as fine white

[1] Challenger and Allpress, *Trans. Chem. Soc.*, 1921, **119**, 913.

[2] Supniewski and Adams (*loc. cit.*) state that the purification of this compound from the Grignard reaction mixture is difficult owing to the trouble caused by the low-melting solid containing traces of toluene and *m*-bromotoluene. The purest product results when crude tri-*m*-tolylbismuthine is converted into its dichloride and the latter reduced with sodium hydrosulphite. Such a preparation, when recrystallised from ligroin, melts at 68° C.

[3] Stilp, *loc. cit.*

[4] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, **121**, 256.

[5] Supniewski, *loc. cit.*; Supniewski and Adams, *loc. cit.*

[6] Stilp, *loc. cit.*; Supniewski and Adams erroneously claim to be the first investigators to obtain this compound.

[7] Gillmeister, *Ber.*, 1897, **30**, 2843; Stilp, *Inaug. Dissert. Rostock*, 1910.

crystals, M.pt. 168° C., which are easily soluble in chloroform, less soluble in petroleum ether. The melting-point of this substance as prepared by method (1) was given as 190° C.

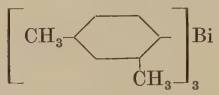
Tri-p-phenetylbismuthine,[1]

forms transparent monoclinic prisms, M.pt. 73° C. Halogen addition products of this substance appear to be unknown.

Tri-p-cumylbismuthine,

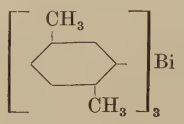
occurs as glistening rhomboidal plates, M.pt. 159° C., readily soluble in chloroform, benzene, ethyl acetate, petroleum or alcohol.

Tri-m-xylylbismuthine,[2]



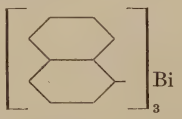
The same methods may be used for the preparation of this derivative as for the tolyl compounds. It crystallises in snow-white felted needles from chloroform-alcohol or benzene-alcohol, M.pt. 173·5° to 175° C. The yield is about 25 per cent., and the compound is readily soluble in benzene, toluene, chloroform or ligroin, soluble with difficulty in alcohol or ether. The *mercurichloride* separates from hot acetic acid in fine needles, M.pt. 160° C.

Tri-p-xylylbismuthine,[3]



is obtained only in 15 per cent. yield using the Grignard method of preparation. Its melting-point is variously given as 193° C. and as 194·5° C. It is a snow-white crystalline substance, readily soluble in chloroform, benzene or ligroin, sparingly soluble in cold alcohol. It decomposes into xylene and bismuth chloride when warmed with concentrated hydrochloric acid; the *m*-compound undergoes similar decomposition in the cold.

Tri-α-naphthylbismuthine,[4]

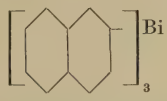


This is prepared by the interaction of α-naphthyl magnesium bromide and bismuth bromide, the product being extracted from the decomposed Grignard residue by chloroform (yield, 60 per cent.). It forms pale

[1] Gillmeister, *loc. cit.*
[2] Stilp, *loc. cit.*
[3] Gillmeister, *loc. cit.*; Stilp, *loc. cit.*
[4] Stilp, *loc. cit.*

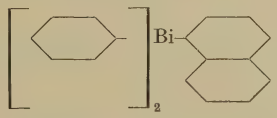
yellow felted needles, M.pt. 234° to 235° C., readily soluble in benzene, toluene, carbon tetrachloride or chloroform, sparingly soluble in ligroin, alcohol or ether. Its *mercurichloride* forms silvery, glistening plates, M.pt. 193° C., soluble in chloroform or acetic acid, insoluble in alcohol or ether. The bismuthine reacts with thallic chloride in ether solution yielding di-α-naphthylchlorobismuthine and thallium di-α-naphthyl chloride.[1]

Tri-β-naphthylbismuthine,



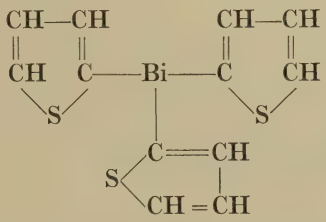
results when the α-bromonaphthalene in the foregoing preparation is replaced by β-bromonaphthalene. It separates as white, glistening crystals, M.pt. 89° C., soluble in benzene, ligroin, chloroform, alcohol or ether.

Diphenyl-α-naphthylbismuthine,[2]



may be isolated (1) by treating α-naphthyl magnesium bromide with diphenylbromobismuthine, (2) from phenyl magnesium bromide and α-naphthyldibromobismuthine, (3) when triphenylbismuthine (2 mols.) and tri-α-naphthylbismuthine (1 mol.) are heated together at 190° C. for two hours. The compound melts at 118° to 119° C., and is readily soluble in benzene, chloroform or toluene, less soluble in alcohol or ether. With warm concentrated hydrochloric acid it yields benzene and naphthalene.

Tri-α-thienylbismuthine,[3]



occurs in 60 per cent. yield when 20 grams of α-iodothiophene, 3 grams of magnesium and 6 grams of bismuth trichloride in 30 c.c. of ether, are allowed to react in 100 c.c. of ether. After boiling for two hours to complete the reaction, the mixture is allowed to stand overnight, then worked up in the usual manner. A slightly better yield results when α-bromothiophene is used. The bismuthine separates as rhombic crystals, M.pt. 137·5° C. (corr.), only sparingly soluble in ether, insoluble in petroleum ether. The product is best crystallised by solution in a little warm benzene and addition of four parts of petroleum ether. It slowly undergoes oxidation in the presence of air.

[1] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, **121**, 256.
[2] Challenger, *Trans. Chem. Soc.*, 1914, **105**, 2210.
[3] Krause and Renwanz, *Ber.*, 1929, **62**, [B], 1710.

Aromatic Compounds of the Types $RBiX_2$ and R_2BiX.

Phenyldibromobismuthine,[1]

When 1·5 grams of triphenylbismuthine in ether are treated with 3 grams of bismuth bromide in the same solvent, yellow crystals of the dibromobismuthine are deposited. These, when recrystallised from benzene, melt at 202° C. The same compound when prepared from diphenylbromobismuthine by the addition of one molecular proportion of bromine in dry chloroform, melts at 205° to 206° C.

p-Chlorophenyldibromobismuthine,[2]

is the decomposition product formed when di-*p*-chlorophenylbromobismuthine is boiled in benzene ; a poor yield also occurs when tri-*p*-chlorophenylbismuthine is treated with bismuth bromide :

$$(C_6H_4Cl)_3Bi + BiBr_3 = (C_6H_4Cl)_2BiBr + C_6H_4Cl.BiBr_2$$
$$2(C_6H_4Cl)_2BiBr = C_6H_4Cl.BiBr_2 + Bi(C_6H_4Cl)_3$$

The bismuthine is only slightly soluble in hot benzene or hot chloroform, and almost insoluble in all other solvents. It decomposes on standing for a few hours.

p-Tolyldichlorobismuthine,[3]

obtained from tri-*p*-tolylbismuthine and bismuth chloride, separates from benzene as yellow needles, M.pt. 206° to 207° C., almost insoluble in most organic solvents. It is decomposed by alcohol or moist solvents and with hydrochloric acid forms toluene and bismuth chloride. During its preparation di-*p*-tolylchlorobismuthine is also obtained.

α-Naphthyldibromobismuthine,

may be prepared from tri-α-naphthylbismuthine (1 mol.) and bismuth bromide (1 mol.) in ether solution, or by heating dry tri-α-naphthylbismuthine dibromide for half an hour at 100° C., moisture being excluded. The compound forms deep orange crystals, M.pt. 208° C., is soluble with difficulty in benzene and practically insoluble in other solvents.

[1] Challenger, *Trans. Chem. Soc.*, 1914, **105**, 2210; *Proc. Chem. Soc.*, 1914, p. 229 ; Challenger and Allpress, *Trans. Chem. Soc.*, 1921, **119**, 919.

[2] Challenger and Ridgway, *Trans. Chem. Soc.*, 1922, **121**, 104.

[3] Challenger and Allpress, *Trans. Chem. Soc.*, 1921, **119**, 913.

Diphenylchlorobismuthine,[1]

When an ether solution of triphenylbismuthine is treated with bismuth chloride in the same solvent, the monochlorobismuthine is deposited as colourless crystals, M.pt. 184° to 185° C., readily soluble in dry chloroform, benzene or toluene, but only slightly soluble in light petroleum or ether. The compound also results when iodine monochloride acts on triphenylbismuthine or diphenyl-α-naphthylbismuthine.[2] Traces of moisture cause decomposition, and it is therefore essential to recrystallise the bismuthine from specially dried solvents.

Diphenylbromobismuthine, $(C_6H_5)_2BiBr$,[3] may be obtained by the foregoing methods, or by the interaction of lead tetraphenyl and bismuth bromide:[4]

$$(C_6H_5)_4Pb + BiBr_3 = (C_6H_5)_2PbBr_2 + (C_6H_5)_2BiBr$$

It is a heavy yellow powder, M.pt. 157° to 158° C., readily soluble in dry chloroform, but not soluble in ether, and decomposed by alcohol, which converts it into bismuth oxybromide. Triphenylbismuthine dibromide, when boiled with dry benzene, gives a good yield of diphenylbromobismuthine.

Diphenyliodobismuthine, $(C_6H_5)_2BiI$.[5]—This compound occurred as the result of an attempt to prepare triphenylbismuthine di-iodide from triphenylbismuthine and iodine:

$$(C_6H_5)_3Bi + I_2 = (C_6H_5)_2BiI + C_6H_5I$$

It forms yellow needles, M.pt. 133° C., which may be recrystallised unchanged from dry chloroform, benzene or acetic acid, but are decomposed by moisture, yielding bismuth oxyiodide and benzene:

$$(C_6H_5)_2BiI + H_2O = 2C_6H_6 + BiOI$$

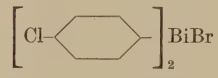
Diphenylcyanobismuthine, $(C_6H_5)_2BiCN$.—When triphenylbismuthine and cyanogen iodide ($1\frac{1}{4}$ mols.) are refluxed in benzene, the cyano-derivative is isolated as small transparent needles melting with decomposition at 210° C. The same product is obtained when an aqueous alcohol solution of triphenylbismuthine dichloride is heated with potassium cyanide.[6] It is sparingly soluble in benzene or alcohol and practically insoluble in ether or light petroleum. If its alcohol solution be concentrated, the compound is decomposed, triphenylbismuthine being produced.

Diphenylthiocyanobismuthine, $(C_6H_5)_2BiCNS$, obtained from triphenylbismuthine dichloride and lead thiocyanate, forms pale yellow crystals of the monoclinic system; the axial ratios $a : b : c = 2{\cdot}4969 : 1 : 3{\cdot}0590$, and the axial angle $\beta = 75° 54'$. It melts at 122° to 122·5° C.

[1] Michaelis and Reese, *Annalen*, 1886, **233**, 58.
[2] Challenger and Allpress, *loc. cit.*
[3] Michaelis and Marquardt, *Annalen*, 1889, **251**, 327.
[4] Goddard, Ashley and Evans, *Trans. Chem. Soc.*, 1922, **121**, 978.
[5] Gillmeister, *Ber.*, 1897, **30**, 2843; Challenger and Allpress, *Trans. Chem. Soc.*, 1915, **107**, 16.
[6] Challenger and Wilkinson, *Trans. Chem. Soc.*, 1922, **121**, 91.

and is soluble in the usual organic solvents with the exception of light petroleum.

Di-p-chlorophenylbromobismuthine,[1]



occurs together with *p*-chlorophenyldibromobismuthine when tri-*p*-chlorophenylbismuthine (2 mols.) in dry ether is treated with a similar solution of bismuth bromide (1 mol.). When crystallised from ether it melts at 159° C., and is readily decomposed by water and moist solvents. Warm alcoholic ammonia regenerates the tri-*p*-chlorophenylbismuthine. A solution of the bromo-derivative in hot dry benzene deposits a yellow solid, M.pt. 244° C.

Di-p-chlorophenyliodobismuthine, $(C_6H_4Cl)_2BiI$, results from the interaction of iodine and tri-*p*-chlorophenylbismuthine. It is a yellow solid, M.pt. 113° C., readily soluble in chloroform or ether. On recrystallisation from chloroform-light petroleum, dry solvents (free from alcohol) being used, a red solid containing organic matter and readily soluble in most solvents is deposited with yellow crystals melting at 139° C.

Di-p-tolylchlorobismuthine,[2]

obtained in the usual manner, crystallises from dry chloroform-ether in transparent crystals, M.pt. 181° C., moderately soluble in hot benzene or chloroform, and almost insoluble in ether or light petroleum.

Di-α-naphthylchlorobismuthine, $(C_{10}H_7)_2BiCl$, forms fine yellow needles, M.pt. 168° C., moderately soluble in dry benzene or chloroform, but only soluble to a slight extent in light petroleum or ether. The compound is extremely susceptible to traces of moisture, and even after keeping for a short time in a closed vessel loses its yellow colour and smells of naphthalene.

Aromatic Compounds of the Type R_3BiX_2.

Triphenylbismuthine difluoride,[3]

When triphenylbismuthine dichloride is boiled with excess of potassium fluoride in alcoholic solution containing a little water, the dichloride gradually disappears and is replaced by the difluoride. The latter melts at 158·5° to 159° C., is readily soluble in chloroform, acetone or ether, but less soluble in light petroleum. The crystals, which belong to the monoclinic system, give the axial ratios $a : b : c = 2{\cdot}0201 : 1 : 1{\cdot}1163$, and the axial angle $\beta = 85° 42'$. The fluorine may be removed from the compound by boiling with calcium or barium oxide in aqueous solution, and with sulphuric acid hydrogen fluoride is liberated.

[1] Challenger and Ridgway, *loc. cit.* [2] Challenger and Allpress, *loc. cit.*
[3] Challenger and Wilkinson, *Trans. Chem. Soc.*, 1922, **121**, 91.

Triphenylbismuthine dichloride, $(C_6H_5)_3BiCl_2$,[1] occurs when chlorine is passed into a solution of triphenylbismuthine in ether, petroleum ether, chloroform or carbon tetrachloride. It crystallises in stout needles, M.pt. 126° C., soluble in alcohol, chloroform or benzene, practically insoluble in ether or petroleum ether. Moist silver oxide, alcoholic potassium hydroxide,[2] potassium cyanate and other inorganic salts react with the dichloride giving varying yields of triphenylbismuthine. When a chloroform solution of the dichloride is treated with moist ammonia, one chlorine atom is removed and triphenylbismuthine hydroxychloride results. When the dichloride is added to concentrated sulphuric acid it yields triphenylbismuthine sulphate and hydrogen chloride is evolved. A dry benzene solution of the dichloride when boiled undergoes partial decomposition with formation of diphenylchlorobismuthine.

Triphenylbismuthine dibromide, $(C_6H_5)_3BiBr_2$, is obtained by direct bromination of triphenylbismuthine. It melts at 122° C., and the value 123° to 124° C. has also been recorded, the rate of heating appearing to account for the discrepancy. It forms yellow crystals which are unstable in the presence of moisture, and even when heated at 100° C. for twenty minutes in a sealed tube the odour of bromobenzene is apparent. When boiled in dry benzene, diphenylbromobismuthine is produced, and with moist ammonia the hydroxybromide is obtained. With ammoniacal hydrogen sulphide bismuth sulphide is quantitatively precipitated. If the dibromide is treated with the Grignard reagent, compounds of the types R_3Bi and R_2BiX are isolated.

Triphenylbismuthine hydroxychloride, $(C_6H_5)_3Bi(OH)Cl$.[3]—When the corresponding dichloride is dissolved in chloroform containing a little light petroleum and moist ammonia is passed in, a white solid is deposited. This is collected and washed first with cold water and then with hot water to remove the ammonium chloride formed. The hot water produces effervescence and evolution of chloroform, which is apparently present as "chloroform of crystallisation." The pure compound is a white powder, M.pt. 160° to 161° C., completely soluble in cold chloroform, hot alcohol or nitrobenzene, moderately soluble in benzene, xylene, acetone or ether, and insoluble in water or light petroleum. When treated with methyl magnesium iodide only triphenylbismuthine and its dichloride are obtained.

Triphenylbismuthine hydroxybromide, $(C_6H_5)_3Bi(OH)Br$, is prepared by the method detailed for the preceding compound. It is a yellow powder, M.pt. 147° to 148° C., resembling the hydroxychloride in solubility.

Triphenylbismuthine dinitrate, $(C_6H_5)_3Bi(NO_3)_2$,[4] is deposited when alcohol solutions of the dichloride or dibromide and silver nitrate are mixed, filtered, and the filtrate concentrated. It crystallises in colourless needles which explode on heating and are soluble in chloroform or benzene, less soluble in cold alcohol. With hydrochloric acid the dichloride is regenerated.

Triphenylbismuthine carbonate, $(C_6H_5)_3BiCO_3$.[5]—Triphenyl-

[1] Michaelis and Marquardt, *Annalen*, 1889, 251, 323.
[2] Challenger and Goddard, *Trans. Chem. Soc.*, 1920, 117, 762.
[3] Challenger and Goddard, *ibid.*
[4] Michaelis and Marquardt, *Annalen*, 1889, 251, 323.
[5] Michaelis and Marquardt, *ibid.*; Challenger and Goddard, *Trans. Chem. Soc.*, 1920, 117, 766.

bismuthine dibromide is suspended in alcohol and treated with an excess of solid sodium hydroxide, the whole being vigorously shaken during the operation. Carbon dioxide is then passed through the solution, the precipitate filtered off, washed with cold water and then boiled with water until a test portion of the liquor is halogen-free. The carbonate is a white powder, insoluble in organic solvents and yielding other salts with acids, carbon dioxide being evolved.

Triphenylbismuthine diacetate, $(C_6H_5)_3Bi(OCOCH_3)_2$[1].—Triphenylbismuthine carbonate is dissolved in hot glacial acetic acid, the solution cooled and treated with water. A white precipitate is obtained which melts at 162° C. and is completely soluble in warm ethyl acetate, cold chloroform, nitrobenzene or warm xylene, moderately soluble in warm benzene, acetone, carbon tetrachloride or alcohol, insoluble in water or light petroleum. If the acetic acid solution of the acetate is allowed to stand for several days without the addition of water, long transparent needles separate, which soften at 130° C. and melt at 136° to 137° C. This substance is an *acid acetate*, $2C_{22}H_{21}O_4Bi.C_2H_4O_2$, and when triturated with water the normal acetate (M.pt. 162° C.) is obtained, which, if dissolved in acetic acid and allowed to crystallise, again yields the acid acetate.

Triphenylbismuthine sulphate, $(C_6H_5)_3BiSO_4$.—The corresponding dichloride is dissolved in concentrated sulphuric acid, the temperature being maintained at about 10° C., and after drawing air through the solution to remove hydrogen chloride, the mixture is poured on ice. The solid is well washed with water and extracted with boiling chloroform. The sulphate is a white solid, not melting at 300° C., and practically insoluble in organic solvents.

Dinitrotriphenylbismuthine dinitrate, $(C_6H_4NO_2)_2(C_6H_5)Bi(NO_3)_2$,[2] is isolated by nitrating triphenylbismuthine dinitrate or dichloride with " mixed acid " (2 parts H_2SO_4 : 1 part HNO_3), efficiently cooling the mixture. The mixed nitro-compounds thus obtained are extracted with hot chloroform, and from 10 grams of the mixed compounds 3 grams of the pure dinitro-compound result. It crystallises from chloroform in pale yellow prisms which explode at about 150° C. and are soluble in acetic acid, but insoluble in ether, petroleum ether or carbon disulphide. It soon decomposes in contact with cold alcohol, the odour of nitrobenzene becoming apparent. The addition of ammonium sulphide to an alcoholic ammonia solution of the nitro-compound causes complete decomposition.

Dinitrotriphenylbismuthine dichloride, $(C_6H_4NO_2)_2(C_6H_5)BiCl_2$, occurs when the foregoing compound in acetic acid solution is treated dropwise with concentrated hydrochloric acid. The white precipitate which is formed is filtered off, washed with water and crystallised from benzene, fine needles, M.pt. 136° C., being deposited. On rapid heating the compound explodes. It dissolves readily in chloroform or benzene, is sparingly soluble in ether or acetic acid, insoluble in petroleum ether. When treated with ammonium sulphide it decomposes.

Trinitrotriphenylbismuthine dinitrate, $(C_6H_4NO_2)_3Bi(NO_3)_2$.[3] —To 100 c.c. of fuming nitric acid, previously cooled to 0° C., 10 grams

[1] Challenger and Goddard, *loc. cit.*

[2] Gillmeister, *Ber.*, 1897, 30, 2843.

[3] Supniewski, *Rocz. Chem.*, 1925, 5, 298; Supniewski and Adams, *J. Amer. Chem. Soc.*, 1926, 48, 507.

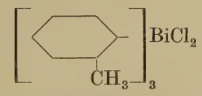
of triphenylbismuthine dinitrate are added and the mixture placed in an ice-chest for twelve hours. The precipitate then produced by pouring the solution into 500 c.c. of ice water is filtered off, washed with water, dried and recrystallised from ethyl acetate. A pale yellow product results, which explodes when heated at about 147° C. Further recrystallisation from acetic acid lowers the melting-point to about 140° C., and the compound no longer explodes. Subsequent crystallisations cause further falls in the melting-point, indicating decomposition of the compound.

Trinitrotriphenylbismuthine dichloride, $(C_6H_4NO_2)_3BiCl_2$, occurs when the preceding compound in acetone is boiled with concentrated hydrochloric acid. The dichloride is precipitated by the addition of a large bulk of water, dried, and recrystallised from ethyl acetate, when it melts at 132° to 134° C.

Triphenylbismuthine dicyanate, $(C_6H_5)_3Bi(OCN)_2$.[1]—The corresponding dichloride (1 mol.) and silver cyanate (2 mols.) are shaken together in dry ether for four hours. The insoluble residue is extracted with chloroform and the resulting solid is twice crystallised from chloroform-light petroleum, the product melting at 128·5° to 129° C. The dicyanate evolves ammonia when warmed with aqueous alcohol (1 : 1), and when heated to 150° C. it decomposes, yielding a pungent oil.

Triphenylbismuthine dibenzoate, $(C_6H_5)_3Bi(OCOC_6H_5)_2$, is the product of reaction between triphenylbismuthine and benzoyl peroxide or between triphenylbismuthine dichloride and silver benzoate. It is a pale yellow solid, M.pt. 171·5° C.

Tri-o-tolylbismuthine dichloride,[2]



occurs when dry chlorine is passed into an ice-cooled solution of tri-*o*-tolylbismuthine in alcohol. It separates from alcohol-chloroform as white, rhombic crystals, M.pt. 162° C., soluble in warm benzene, chloroform or acetic acid, insoluble in cold alcohol or petroleum ether.

Tri-o-tolylbismuthine dibromide, $(C_6H_4.CH_3)_3BiBr_2$, separates from benzene in pale yellow needles, M.pt. 127° C., slowly decomposing in the air.

Tri-o-tolylbismuthine dinitrate, $(C_6H_4.CH_3)_3Bi(NO_3)_2$,[3] is prepared in the usual manner and decomposes with explosion and without melting on heating. It separates from chloroform or benzene in rhombic crystals.

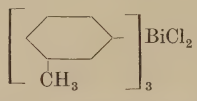
Trinitrotri-o-tolylbismuthine dichloride, $(CH_3.C_6H_3.NO_2)_3BiCl_2$.[4]—A mixture of 10 grams of dry tri-*o*-tolylbismuthine dichloride and 10 grams of finely powdered silver nitrate is dissolved in 60 c.c. of fuming nitric acid at 0° C. After twelve hours water is added, the precipitate filtered off and extracted with acetone to remove organic matter from the silver chloride. The acetone solution is boiled with hydrochloric acid and the precipitate which forms is recrystallised

[1] Challenger and Wilson, *J. Chem. Soc.*, 1927, p. 209.
[2] Gillmeister, *Ber.*, 1897, **30**, 2843; Stilp, *Inaug. Dissert. Rostock*, 1910.
[3] Gillmeister, *loc. cit.*
[4] Supniewski and Adams, *loc. cit.*

from ethyl acetate. The product thus obtained melts at 149° to 150° C. and is very unstable, decomposing on standing and always possessing an odour of nitrotoluene.

Tri-o-carboxytriphenylbismuthine dichloride, $(C_6H_4.COOH)_3BiCl_2$, is the oxidation product of tri-*o*-tolylbismuthine dichloride using chromic acid in glacial acetic acid solution at 68° to 70° C. for the purpose of oxidation. The yield is only about 15 per cent. The product is white and melts at 157° to 159° C.

Tri-m-tolylbismuthine dichloride,

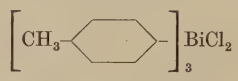


obtained in the usual manner, separates from acetone as white crystals, M.pt. 132° to 133° C.

Tri-m-tolylbismuthine dibromide, $(C_6H_4.CH_3)_3BiBr_2$, melts at 52° C., and cannot be purified by crystallisation, as it rapidly decomposes in the air.[1]

Tri-m-tolylbismuthine diacetate, $(C_6H_4.CH_3)_3Bi(OCOCH_3)_2$.—A solution of 10 grams of tri-*m*-tolylbismuthine dihalide in 150 c.c. of glacial acetic acid is heated under reflux with an excess of a saturated solution of lead acetate in glacial acetic acid. The lead halide is filtered off and the filtrate, on cooling, deposits white crystals. Purification from acetone gives a product of melting-point 148° to 149° C.

Tri-p-tolylbismuthine dichloride,[2]



crystallises in fine white needles from chloroform-alcohol, M.pt. 147° C., readily soluble in benzene, chloroform or hot alcohol, but sparingly soluble in ether, petroleum ether or cold alcohol.

Tri-p-tolylbismuthine hydroxychloride, $(CH_3.C_6H_4)_3Bi(OH)Cl$, is obtained by prolonged boiling of the foregoing dichloride in very dilute alcohol. It is a white crystalline powder, M.pt. 154° C. with decomposition.

Tri-p-tolylbismuthine dibromide, $(CH_3.C_6H_4)_3BiBr_2$, crystallises in glistening yellow needles from a mixture of benzene and alcohol. It melts at 111° to 112° C. and has a similar solubility to the corresponding phenyl compound.

Tri-p-tolylbismuthine hydroxybromide, $(CH_3.C_6H_4)_3Bi(OH)Br$, is a yellow powder, M.pt. 140° C.

Tri-p-tolylbismuthine dinitrate, $(CH_3.C_6H_4)_3Bi(NO_3)_2$, prepared in a similar manner to the phenyl compound, forms glistening needles or leaflets, exploding on heating and readily soluble in chloroform, sparingly soluble in alcohol.

Tri-p-tolylbismuthine diacetate, $(CH_3.C_6H_4)_3Bi(OCOCH_3)_2$,[3] is obtained by a similar method to that detailed for the corresponding *meta*-compound. It forms white crystals, M.pt. 162° C.

[1] Challenger and Pritchard (*Trans. Chem. Soc.*, 1924, 125, 869) give the melting-point as 92° C.

[2] Michaelis and Marquardt, *loc. cit.*; Supniewski, *loc. cit.*

[3] Supniewski and Adams, *loc. cit.*

Tri-p-carboxytriphenylbismuthine dichloride, $(C_6H_4.COOH)_3BiCl_2$.—A solution of 2·2 grams of tri-*p*-tolylbismuthine dichloride in 30 c.c. of acetone is prepared, and also a 2·5 per cent. aqueous solution of 4·4 grams of potassium permanganate. These two solutions are added alternately in small quantities at a time to 50 c.c. of water in a flask until the reaction is complete. During the operation the temperature must be kept below 20° C. The reaction mixture is finally shaken for half an hour, filtered from manganese dioxide, and the organic matter precipitated from the filtrate by the addition of 10 per cent. hydrochloric acid. The yield is about 1 gram, and the melting-point 130° C. When the compound is dissolved in water containing sodium or potassium hydroxide, the addition of acetone or alcohol precipitates the corresponding alkali salt in crystalline form.

Tri-p-carbomethoxytriphenylbismuthine dichloride, $(C_6H_4.CO_2CH_3)_3BiCl_2$, occurs when the foregoing acid in absolute methyl alcohol saturated with hydrogen chloride is allowed to stand for two hours. The yield is poor and the product forms white crystals from methyl alcohol, M.pt. 103° C., which precipitate bismuth hydroxide on warming with alcohol.

Trinitrotri-p-tolylbismuthine dinitrate, $(CH_3.C_6H_3.NO_2)_3Bi(NO_3)_2$.—This is prepared in a similar manner to the phenyl compound, by nitrating tri-*p*-tolylbismuthine dinitrate. The nitration requires two hours at room temperature. The product is a white crystalline powder, which, after crystallisation from acetone or ethyl acetate, explodes at about 160° C.

Trinitrotri-p-tolylbismuthine dichloride, $(CH_3.C_6H_3.NO_2)_3BiCl_2$, isolated in the usual manner, is a white powder, which can be purified from acetone, and melts at 156° C.

Trinitrotri-p-carbomethoxytriphenylbismuthine dinitrate, $(NO_2.C_6H_3.CO_2CH_3)_3Bi(NO_3)_2$, is formed by nitration with fuming nitric acid at 0° C., and separates from acetone as a white crystalline powder which explodes at 150° to 160° C.

Trinitrotri-p-carboxytriphenylbismuthine dichloride, $(NO_2.C_6H_3.CO_2H)_3BiCl_2$, occurs when the foregoing dinitrate is boiled for an hour with 10 per cent. hydrochloric acid. The product is filtered off, dissolved in acetone and boiled with concentrated hydrochloric acid. As the solution cools a white precipitate is deposited, which is purified by crystallisation from acetone. It melts with decomposition at 250° to 260° C.

Tri-o-anisylbismuthine dichloride, $(CH_3O.C_6H_4)_3BiCl_2$,[1] prepared by passing chlorine into a solution of tri-*o*-anisylbismuthine in dry carbon tetrachloride, is a white crystalline substance, M.pt. 174° C.

Tri-o-anisylbismuthine dibromide, $(CH_3O.C_6H_4)_3BiBr_2$, M.pt. 101° C., cannot be recrystallised owing to its tendency to change to the hydroxybromide. It is readily soluble in benzene, ligroin or chloroform, sparingly soluble in alcohol, insoluble in ether or petroleum ether.

Tri-p-anisylbismuthine dichloride, $(CH_3O.C_6H_4)_3BiCl_2$,[2] is readily soluble in benzene or chloroform and melts at 133° C., but treatment with alcohol causes decomposition with formation of bismuth oxychloride.

Tri-p-anisylbismuthine dibromide, $(CH_3O.C_6H_4)_3BiBr_2$, has a

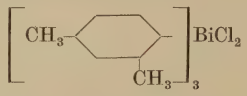
[1] Stilp, *loc. cit.* [2] Gillmeister, *loc. cit.*

similar solubility to the foregoing dichloride. It forms yellow needles, M.pt. 103° C. It is not decomposed by boiling alcohol, and is stable in air. Ammonium sulphide decomposes it with formation of bismuth sulphide.

Tri-p-cumylbismuthine dichloride, $(C_3H_7.C_6H_4)_3BiCl_2$, prepared in the usual manner, melts at 208° C. and is soluble in most organic solvents.

Tri-p-cumylbismuthine dibromide, $(C_3H_7.C_6H_4)_3BiBr_2$, melts at 150° C.

Tri-m-xylylbismuthine dichloride,[1]

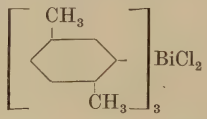


obtained by the chlorination of the bismuthine in dry ether, chloroform or carbon tetrachloride, forms small, glistening prisms, M.pt. 161° C.

Tri-m-xylylbismuthine dibromide, $[(CH_3)_2C_6H_3]_3BiBr_2$, occurs when the components are brought together in petroleum ether. It separates from alcohol-benzene in fine needles, M.pt. 117° C.

Tri-m-xylylbismuthine hydroxybromide, $[(CH_3)_2C_6H_3]_3Bi(OH)Br$,[2] is isolated when the bromination of tri-*m*-xylylbismuthine is carried out in alcohol instead of in petroleum ether. Crystallisation from alcohol-benzene yields a pale yellow crystalline powder, melting at 250° C. with marked decomposition.

Tri-p-xylylbismuthine dichloride,[3]



crystallises in fine white needles, M.pt. 167·5° C. If its chloroform or benzene solution be treated with warm alcohol, decomposition gradually takes place with deposition of bismuth oxychloride.

Tri-p-xylylbismuthine dibromide, $[(CH_3)_2C_6H_3]_3BiBr_2$, yields warty yellow needles, M.pt. 130° C., which are affected by heating with alcohol in the same way as the dichloride.

Tri-α-naphthylbismuthine dichloride,[4]

The chlorination of tri-α-naphthylbismuthine is carried out in dry chloroform and the dichloride precipitated by the addition of light petroleum. Crystallisation from chloroform-petroleum gives a product melting sharply at 166° C. It is a yellow, crystalline powder, readily soluble in chloroform, moderately soluble in acetone or benzene, and insoluble in light petroleum. Heating for several hours at 100° C. does not affect it, and it is also stable towards hydrochloric acid. When

[1] Michaelis and Marquardt, *loc. cit.*
[2] Stilp, *loc. cit.*
[3] Gillmeister, *loc. cit.*
[4] Challenger and Goddard, *Trans. Chem. Soc.*, 1920, **117**, 772.

shaken with a suspension of silver oxide in moist acetone the two atoms of chlorine are removed.

Tri-α-naphthylbismuthine dibromide, $(C_{10}H_7)_3BiBr_2$,[1] is prepared by the bromination of the bismuthine in dry chloroform. It is precipitated by the addition of an excess of dry ether, and crystallisation from dry benzene-absolute alcohol gives a yellow crystalline powder, M.pt. 124° C., readily soluble in benzene or chloroform, sparingly soluble in cold alcohol, insoluble in ether. It tends to lose bromonaphthalene on warming at 100° C., and when treated with phenyl magnesium bromide (2 mols.) it gives principally tri-α-naphthylbismuthine and traces of diphenyl-α-naphthylbismuthine, but when only one equivalent of Grignard reagent is used unchanged dibromide and α-naphthyldibromobismuthine are the only products isolated. Methyl magnesium iodide merely removes the bromine from the dibromide, and mercury diphenyl yields tri-α-naphthylbismuthine and a little diphenyl-α-naphthylbismuthine.[2]

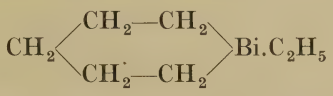
Diphenyl-α-naphthylbismuthine dichloride, $(C_6H_5)_2(C_{10}H_7)BiCl_2$,[3] separates in pale yellow crystals from dry alcohol-free chloroform on the addition of light petroleum, M.pt. 141° to 142° C., insoluble in acetone. Moist silver oxide in acetone suspension removes the chlorine atoms.

Diphenyl-α-naphthylbismuthine dibromide, $(C_6H_5)_2(C_{10}H_7)BiBr_2$,[4] M.pt. 141° to 142° C., forms pale yellow crystals from chloroform-petroleum solution, which are insoluble in acetone. The halogen is removed by moist silver oxide, the bismuthine being regenerated.

ω-Tristyrylbismuthine,[5] $(C_6H_5CH:CH)_3Bi$, has been isolated only in very small quantity, and its physical constants have not been determined. The scheme for the production of this derivative is as follows: $C_6H_5.CH:CHCOOH \longrightarrow C_6H_5.CHBr.CHBr.COOH \longrightarrow C_6H_5.CH:CHBr \longrightarrow C_6H_5.CH:CHMgBr \longrightarrow (C_6H_5.CH:CH)_3Bi$. During the preparation some diphenylbutadiene is produced.

Heterocyclic Systems containing Bismuth.[6]

Ethylcyclopentamethylene bismuth,

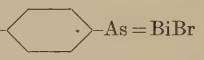


This compound is produced by the interaction of ethyldibromobismuthine and the Grignard reagent derived from 1 : 5-dibromopentane. It is a viscous oil, distilling at 108° to 112° C., heavier than water and possessing an unpleasant and persistent odour. It becomes turbid in the presence of traces of oxygen, is actively oxidised in the air, igniting readily. If a piece of paper be saturated with the oil, it inflames after a few seconds, emitting dense yellow fumes.

[1] Stilp, *loc. cit.*
[2] Challenger and Allpress, *Trans. Chem. Soc.*, 1921, **119**, 913.
[3] Challenger and Wilkinson, *Trans. Chem. Soc.*, 1922, **121**, 91.
[4] Challenger and Goddard, *Trans. Chem. Soc.*, 1920, **117**, 772.
[5] Fabrykant, *Bull. pharm. Inst. Poland*, No. 2, 1927, p. 1.
[6] Grüttner and Wiernik, *Ber.*, 1915, **48**, 1473.

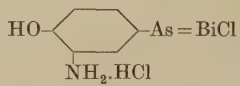
Arsenic-Bismuth Derivatives.

4-Acetylaminophenylarsenobismuth bromide,[1]



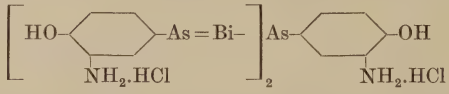
4-Acetylaminophenylarsine (2·1 parts) is dissolved in 30 parts of methyl alcohol containing hydrogen bromide, and 4·5 parts of bismuth tribromide in methyl alcohol added. Addition of ether precipitates a heavy black powder, decomposed by acids and alkalis.

3-Amino-4-hydroxyphenylarsenobismuth chloride hydrochloride,



This derivative is obtained by condensing 3-amino-4-hydroxyphenylarsine with bismuth chloride in methyl alcohol solution in the presence of hydrogen chloride. It is a black powder, decomposing in a similar manner to the preceding compound, and even boiling its aqueous solution leads to decomposition.

Tris-3-amino-4-hydroxyphenylarsenodibismuth dihydrochloride,[2]



This compound is prepared by mixing 3-amino-4-hydroxyphenylarsine in methyl alcohol with a similar solution of bismuth trichloride. It is black in colour, its aqueous solutions are decomposed on boiling, and hydrogen peroxide in alkaline solution instantly causes decomposition, with formation of 3-amino-4-hydroxyphenylarsinic acid and bismuth oxide.[3]

The Determination of Bismuth in Pentavalent Bismuth Compounds.[4]

The substance (0·2–0·3 gram) is treated with about 10 c.c. of an ammoniacal solution of hydrogen sulphide and the mixture evaporated to dryness in an air-bath at 115° to 125° C., the hydrocarbon formed during the decomposition being driven off and the residue of bismuth sulphide and sulphur boiled for a few minutes with 10 c.c. of concentrated hydrochloric acid. The solution is then filtered, diluted with water, hydrogen sulphide passed in, and the precipitated bismuth sulphide filtered off on a Gooch crucible, washed with carbon disulphide, dried, and weighed.

[1] German Patent, 269745.

[2] Ehrlich and Karrer, *Ber.*, 1913, 46, 3564.

[3] When an alkali bismuth tartrate and the disodium salt of "Salvarsan" are mixed in aqueous solution and the whole poured into ether-methyl alcohol solution, a complex is precipitated which is said to have the general formula, R.As : Bi.As(R).Bi : As.R_1, where R is an aminoaryl radical (American Patent, 1605691).

[4] Challenger and Goddard, *Trans. Chem. Soc.*, 1920, 117, 762.

APPENDIX.

APPENDIX.

Mixed Stibines.[1]

Ethyldi-n-butylstibine, $(C_2H_5)(C_4H_9)_2Sb$.—50 grams of ethyldi-iodostibine in 200 c.c. of ether are added to the Grignard reagent from 12 grams of magnesium and 69 grams of *n*-butyl bromide in 300 c.c. of ether. The preparation is carried out in an atmosphere of hydrogen, the resulting mixture treated with ammonium chloride solution, the ether layer dried, the solvent expelled in a stream of carbon dioxide, and the residual liquid fractionally distilled under reduced pressure. The yield of stibine is about 4 grams. It boils at 147° C. at 43 mm., and the density is 1·155 at 17° C.

The following compounds were prepared in a similar manner to the above stibine : *Ethyldi-n-amylstibine*, B.pt. 167° C. at 51 mm., density 1·094 at 23° C. ; *ethyldicyclohexylstibine*, B.pt. 122°–126° C. at 15 mm., density 0·914 at 13° C. ; *di-o-tolylethylstibine*, B.pt. 196°–210° C. at 10 mm. ; *di-m-tolylethylstibine*, B.pt. 211°–216° C. at 15 mm. ; *di-p-tolylethylstibine*, B.pt. 226° C. at 5 mm.

Tri-isobutylstibine oxide, $(C_4H_9)_3SbO$, occurs when the stibine in alcohol solution is shaken with red mercuric oxide, but air oxidation of the stibine yields a *double oxide*, $(C_4H_9)_3SbO.Sb_2O_3$.

Tri-isobutylstibine dichloride, $(C_4H_9)_3SbCl_2$, obtained in the usual way, crystallises in rhombs from ether or carbon tetrachloride, melting at 91° C. ; the *dibromide*, M.pt. 88° C., forms white rhombic plates from acetone, and the *di-iodide* gives pale yellow crystals melting at 70° C.

Methyltri-isobutylstibonium iodide, $(CH_3)(C_4H_9)_3SbI$, is slowly formed in a concentrated ethereal solution of the stibine and methyl iodide. It melts indefinitely above 155° C. The methiodide and mercuric iodide in hot alcohol form *methyltri-isobutylstibonium mercuri-iodide*, yellow needles, M.pt. 119° C. A *mercurichloride* is known, and a *chloroplatinate*, orange needles, M.pt. 158° C.

Naphthyl Antimony Compounds.[2]

β-Naphthylstibinic acid, $C_{10}H_7.SbO(OH)_2$.—96 grams of β-naphthylamine in 3 litres of 2 per cent. hydrochloric acid are diazotised, and 300 c.c. of 30 per cent. hydrochloric acid added, followed, with continued cooling and stirring, by a solution of 96 grams of antimony trioxide in 300 c.c. of 30 per cent. hydrochloric acid. The precipitate is washed with water and added to 6 litres of *N* sodium hydroxide. It takes about four days for the evolution of nitrogen to be complete,

[1] Brinnand, Dyke, W. H. Jones and W. J. Jones, *J. Chem. Soc.*, 1932, p. 1815.
[2] Brinnand, Dyke, W. H. Jones and W. J. Jones, *loc. cit.*

when the brown by-product is removed, and the filtrate acidified with hydrochloric acid. The precipitated β-naphthylstibinic acid is washed, dissolved in concentrated hydrochloric acid, and excess of solid ammonium chloride added. *Ammonium β-naphthylchloroantimonate* separates as a yellow powder, is washed with concentrated hydrochloric acid, and added to 1 litre of water. The latter effects hydrolysis, and a pale salmon-coloured precipitate of β-naphthylstibinic acid separates. The acid does not melt below 200° C.

β-Naphthylstibinoxide, $C_{10}H_7.SbO$.—A solution of the foregoing compound in concentrated hydrochloric acid is diluted with aqueous methyl alcohol, cooled with ice, saturated with sulphur dioxide, after addition of sodium iodide, and poured after several hours on ice and aqueous ammonia. The oxide separates as a voluminous precipitate, which commences to decompose when heated to 160° C.

Antimonyl *d*-Tartrates.[1]

Tetraethylphosphonium antimonyl d-tartrate is obtained in aqueous solution when equivalents of tetraethylphosphonium iodide and silver antimonyl *d*-tartrate are mixed in solution. The solution is filtered, and the tartrate isolated in quantitative yield by evaporating off the solvent. It forms a white powder, very soluble in water, but insoluble in ether, acetone, benzene, carbon disulphide, or chloroform. By a similar process *tetra-n-propylphosphonium antimonyl d-tartrate* is obtained.

Methyltri-n-propylstibonium antimonyl d-tartrate occurs when the foregoing phosphorus compounds are replaced by methyltri-*n*-propylstibonium iodide. The salt is very soluble in water.

The specific rotations of a number of these antimonyl tartrates have been measured in 2 per cent. aqueous solution, and the molecular rotations are given in the following table. In the third column are the p_H values of $N/100$ aqueous solutions of these salts of antimonyl tartaric acid.

Antimonyl d-tartrate	$[M]_D$	p_H
Tetraethylphosphonium . . .	456·7°	4·0
,, -*n*-propylphosphonium . . .	449·3°	3·8
,, ethylarsonium	467·7°	..
Methyltriethylarsonium . . .	453·9°	4·0
Dimethyldi-*n*-propylarsonium . .	459·0°	4·0
Methyltri- ,, ,, ,, . .	466·7°	3·6
,, ,, amyl ,, . .	457·5°	3·6
,, ,, propylstibonium . .	468·2°	3·2
Potassium	458°	4·0

Tri-*n*-alkylbismuthines.[2]

Tri-n-propylbismuthine, $(CH_3.CH_2.CH_2)_3Bi$.—The Grignard reagent from 61 c.c. of *n*-propyl bromide and 16·2 grams of magnesium in 200 c.c. of ether, is treated with 30 grams of bismuth chloride in 350 c.c. of ether. The preparation is carried out in a hydrogen atmosphere in an apparatus very similar to that described on p. 171. The

[1] Brinnand, Dyke, W. H. Jones and W. J. Jones, *loc. cit.*

[2] Davies, Norvick and W. J. Jones, *Bull. Soc. chim.*, 1931, [4], 49, 187.

bismuthine boils at 86° to 87° C. at 8 mm., and has a density of 1·621 at 17° C.

Tri-n-butylbismuthine, $(CH_3.CH_2.CH_2.CH_2)_3Bi$, is obtained in a similar way to the foregoing compound. The product boils at 124° C. at 7 mm., and has a density of 1·456 at 17° C.

Tri-n-amylbismuthine, $(CH_3.CH_2.CH_2.CH_2.CH_2)_3Bi$, boils at 157° to 158° C. at 7 mm.; density 1·381 at 17° C. This product is distinctly yellow in colour, indicating nascent decomposition.

The following three tables give interesting comparisons of the alkyl derivatives of Group V elements of the Periodic Classification :—

TABLE I.—BOILING POINTS.

	Phosphine	Arsine	Stibine	Bismuthine
Triethyl .	128·3° C. at 760 mm.	141° C. at 760 mm.	160° C. at 760 mm.	107° C. at 79 mm.
Tri-*n*-propyl	103·5° C. ,, 50 ,,	92° C. ,, 27 ,,	100° C. ,, 25 ,,	86°–87° C. at 8 mm.
,, ,, butyl	149·5° C. ,, ,, ,,	150° C. ,, 41 ,,	131° C. ,, 12 ,,	124° C. at 7 mm.
,, ,, amyl .	185·5° C. ,, ,, ,,	179°–180° C. at 31 mm.	168° C. ,, 16 ,,	157°–158° C. at 7 mm.

TABLE II.—BOILING POINTS AT 50 mm.

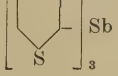
	Phosphine	Arsine	Stibine	Bismuthine
Triethyl .	57° C.	67° C.	83° C.	96° C.
Tri-*n*-propyl	103·5° C.	106° C.	116° C.	127° C.
,, ,, butyl.	149·5° C.	155° C.	167° C.	173° C.
,, ,, amyl .	185·5° C.	193° C.	199° C.	209° C.

TABLE III.—DENSITY IN GRAMS PER C.C.

	Phosphine	Arsine	Stibine	Bismuthine
Triethyl .	0·800 at 18·6° C.	1·150 at 20° C.	1·324 at 16° C.	1·82
Tri-*n*-propyl	0·807 ,, 25° C.	1·031 ,, 17° C.	1·241 ,, 25° C.	1·621 at 17° C.
,, ,, butyl.	0·812 ,, ,,	0·993 ,, 21° C.	1·191 ,, ,,	1·456 ,, ,,
,, ,, amyl .	0·820 ,, ,,	0·980 ,, 18·5° C.	1·136 ,, 18° C.	1·381 ,, ,,

Antimony and Bismuth Thienyl Compounds.[1]

Antimony tri-2-thienyl,



[1] Krause and Renwanz, *Ber.*, 1932, 65, [B], 777.

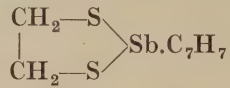
is prepared in a similar manner to the corresponding arsenical compound (this Volume, Part II, p. 413). It is very sensitive to air, and melts at 49° to 49·5° C. Its solution in ether in the presence of air slowly deposits pure antimony oxide. The reaction with hydrogen peroxide seems rather uncertain, but at least one thienyl group is eliminated. A solution of iodine in ether gives 2-iodothiophene and antimony tri-iodide.

Chlorine reacts with antimony tri-2-thienyl to form the *dichloride*, M.pt. 229° C. (corr.) with decomposition. The corresponding *dibromide* melts at 182·5° C. Treatment of these dihalides with potassium hydroxide transforms them into the *oxide*, M.pt. 217° C. (corr.) with decomposition.

Bismuth tri-2-thienyl, $(C_4H_3S)_3Bi$, in benzene solution is not affected particularly by air or hydrogen peroxide. The halogens in carbon tetrachloride solution, however, split out the bismuth completely.

Antimony Derivatives of 1 : 2-Dimercaptoethane.[1]

1-p-Tolylcyclo-2 : 5-dithio-3 : 4-dimethylenestibine,



p-Tolyldichlorostibine (9 grams) and 3 grams of 1 : 2-dimercaptoethane in 30 c.c. of methyl alcohol give 6 grams of precipitate and a further 2·5 grams on standing (total yield, 88 per cent.). The compound is washed with methyl alcohol and recrystallised from light petroleum, when a mixture of long needles and small nodules, M.pt. 90° C., is deposited. The former pass into the latter on standing with the mother liquor. By seeding solutions with either form, the compound easily crystallises in that form alone.

1 : 2-Dimercaptoethane has also been condensed with *p*-carboxyphenyldi-iodostibine (M.pt. 120° to 132° C.), but no definite results have been obtained.

Distillation of some Antimony Derivatives in High Vacua.[2]

Phenyldimethylstibine cyanobromide, $C_6H_5(CH_3)_2Sb.CNBr$, is isolated by slowly adding 18·4 grams of phenyldimethylstibine in 90 c.c. of ether to a solution of 8·5 grams of dry cyanogen bromide in 42 c.c. of ether, the reaction being carried out in a nitrogen atmosphere with good cooling. The cyanobromide which separates, melts at 135° C., and at 150° C. methyl bromide splits out. The residue when rectified in a nitrogen vacuum yields 5 grams of *phenylmethylcyanostibine*, B.pt. 115° to 118° C.

Phenyldimethylstibine reacts with chlorine in carbon tetrachloride solution to give a *dichloride* which, heated *in vacuo*, decomposes at 210° C. into dimethylchlorostibine and diphenylchlorostibine. *Methylcyclopentamethylenestibine*, B.pt. 73° to 73·5° C. at 17 mm., yields a *dichloride*, which decomposes *in vacuo* at 160° to 185° C. into methyl chloride and *antimony cyclopentamethylene chloride*, B.pt. 110° to 111° C. at 13 mm.

[1] Clark, *J. Chem. Soc.*, 1932, p. 1826.
[2] Steinkopf, Schubart and Roch, *Ber.*, 1932, 65, [B], 409.

Miscellaneous Antimony Compounds.

The following derivatives are isolated from the corresponding amines :—[1]

m- and *p-phenylene* and *1 : 4-naphthylene-distibinic acids; diphenylene-pp-(pp-distibinotetraphenylene), 3 : 3-dimethyldiphenylene-4 : 4'-, 3 : 3-dimethoxydiphenylene-4 : 4'-*, and *diphenylmethane-pp-distibinous oxides ; benzophenone-pp-distibinic acid ; diphenyl-m-tolylmethylcarbinol-ppp-tristibinic acid* and *-methane-ppp-tristibinous oxide; stilbene-4 : 4'-distibinic acid* and *distibinous oxide; methylene-* and *ethylenediaminophenylene-4 : 4'-distibinous oxides ; bisphenylazomethine-pp'-distibinous oxide; s-carbohydrazine-diphenylene-pp-distibinic acid; hydrazodicarbonamino-diphenylene-pp-distibinic acid ; hydrazobenzene-* and *benzanilide-pp'-distibinous oxides ; triphenylphosphine-mmm-tristibinic acid, triphenylstibine-mmm-tristibinic acid ; sodium 3-carbobenzyloxy-4-acetamidophenylstibinate,*[2] *sodium 3-carbobenzyloxy-4-propionamidophenylstibinate, sodium 3-carbobenzyloxy-4-isobutyramidophenylstibinate.*

[1] Mistry and Guha, *J. Indian Inst. Sci.*, 1932, 15 A, 25.
[2] Niyogi, *J. Indian Chem. Soc.*, 1931, 8, 59.

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